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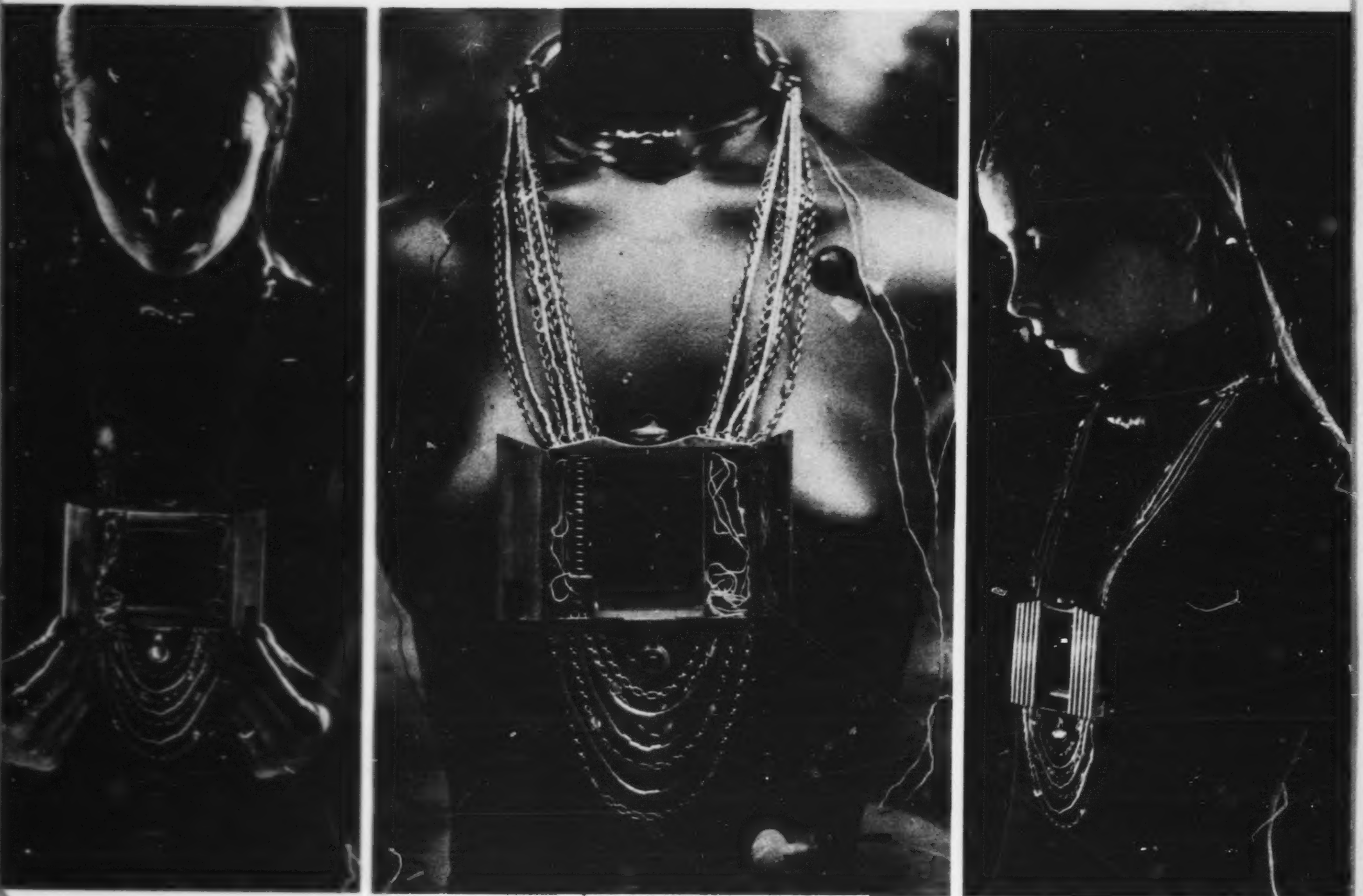
Proceedings of the Symposium on the Development and Usage of Personal Monitors for Exposure and Health Effect Studies



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COVER: A physiologic monitoring device incorporated into a piece of jewlery. The device contains a monitoring electrode that transmits the ECG through electronic circuitry to activate a liquid crystal display of the subject's electrophysiologic heart pattern. The left-hand picture shows the device in an open position; the center picture shows it with the electrodes in place on the body; and the right-hand picture shows the device in a closed position, the configuration in which it is usually worn. (Photos courtesy of Mary Ann Scherr and Dr. George S. Malindzak, Jr.)

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16. ABSTRACT

The work reported herein represents the content of a Symposium to present the state-of-the-art in personal monitor developments for measurement of pollution exposures and physiological responses to pollution exposures. This report contains edited transcripts of the discussion following each paper, the transcript of an informal general discussion period and the transcript of a closing panel discussion.

The breakthroughs in miniaturization of data processing and control modules through usage of digital microcircuitry has allowed a new generation of pocket sized personal monitors to be developed for both pollution variables and physiological measures. The Symposium addresses the conduct of epidemiological and exposure assessment studies which incorporate these monitors into the design.

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Sponsored by
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January 22-24, 1979
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Symposium Chairmen

David T. Mage, Ph.D.

Statistical and Technical Analysis Branch
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Research Triangle Park, North Carolina

and

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Foreword

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment to promote the public health and welfare and the productive capacity of our Nation's population.

The Health Effects Research Laboratory, Research Triangle Park, North Carolina, conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, nonionizing radiation, environmental carcinogenesis, and the toxicology of pesticides, as well as other chemical pollutants. The Laboratory participates in the development and revision of air quality criteria documents on pollutants for which national ambient air quality standards exist or are proposed, provides the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is primarily responsible for providing the health basis for nonionizing radiation standards. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator, to assure the adequacy of health care and surveillance of persons having suffered imminent and substantial endaangerment of their health.

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Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring and Support Laboratory, Research Triangle Park, is responsible for development of: environmental monitoring technology and systems; Agency-wide quality assurance programs for air pollution measurement systems; and technical support to the Agency's operating functions, including the Office of Air, Noise, and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

This conference was conducted by the Environmental Monitoring and Support Laboratory, Research Triangle Park, at the request of the Health Effects Research Laboratory. Thirty-five papers were presented on advances in personal monitor designs and applications. The Environmental Monitoring and Support Laboratory will play a continuing role in their development through programs of field testing, quality assurance, and determination of their equivalence to the EPA-designated instruments for the pollutants to be monitored.

F.G. Hueter, Ph.D.
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Health Effects Research Laboratory

Thomas R. Hauser, Ph.D.
Director
Environmental Monitoring
and Support Laboratory

Opening Remarks

Ralph W. Stacy, Ph.D.
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I trust that no one will dispute my contention that human research on health effects of air pollutants, carried out on controlled and carefully selected cohorts of human subjects under carefully controlled conditions, is entirely necessary in the scheme of research required for the intelligent determination of ambient air standards. This type of research is the primary mission of the Clinical Studies Division of EPA. Our facilities, located here in Chapel Hill, N.C., are among the most sophisticated in the world, and we are currently carrying on a heavy research schedule.

However, none of us at the Clinical Studies Division labors under the delusion that our research will supply all of the answers required for air pollution control. Our highly controlled scientific studies, carried out on selected subject groups with exposures artificially produced in an idealized time pattern, supply the most accurate data available on the response of humans to pollution exposure, but we can never hope to study more than a small and narrowly defined sample of the population. These studies will form a data base that is more accurate and more carefully defined than we could obtain outside the laboratory, and they will probably function as a comparison standard for other types of studies.

Ultimately, however, we must have information on: 1) the response of all segments of the population to pollutant exposure, 2) the amounts and time patterns of pollutant exposures which actually do or are likely to occur in the general population, and 3) the correlation of the exposures that occur with the effects that result. The exposure data and the health effects data must be obtained simultaneously on people who are of all ages, both sexes, well and ill, of all ethnic groups, and in all existing life situations. Only when we have such all-inclusive data can we make assuredly correct, defensible judgments of regulatory requirements. In the final analysis, this is an epidemiological problem, and it is an extremely important and difficult one. I repeat--this problem is a very large one; we dare not treat it lightly.

Recent clinical researches on air pollution effects have made it abundantly clear that humans vary enormously in their physiologic responses to polluting agents. For example, we have shown clearly that in a group of 100 individuals, we can expect that between 15 and 30 of them will be quite sensitive to photochemical oxidants (specifically, ozone). Some 20 to 30 of these persons will not respond at all to the same exposure, and the remainder will respond to some degree. This is actually a very important observation because it means that the usual scientific experiment--in which the means of a number of individuals in a control group and an experimental group are compared--is simply not applicable to a true understanding of pollutant effects. We expect this variability to become a great deal more apparent when we expand our studies to include the very young, the old, the ill, and so on. This means, of course, that we must re-examine our epidemiological and statistical techniques, and that we must be sure that they are adequate.

We have also shown clearly that pollutant health effects often are not synchronized in time with pollutant exposure. An effect may be delayed, or, with continued exposure, an effect may be appreciably reduced or even eliminated entirely. Thus, we need continuous measurements over extended time periods, and this imposes additional methodological requirements.

In addition, we are now able to identify some health effects data which are significant indicators of pollutant-produced health decrements; others are now known to contribute little to the identification of hazards; and there are some whose significance has not been tested. Thus, we have some homework to do before we can head into the final design of measuring devices.

All of this simply means that the kind of information we really must have is a total picture of pollutant exposure and health effects in the general population, measured under normal living conditions. This leads us directly to the conclusion that the measuring instrument must accompany the monitored individual wherever he or she goes and in whatever he or she does. It is not enough to measure one-time health status of members of the population and to compare these effects with pollutant exposure patterns obtained at some fixed measurement station years or blocks or miles away.

It means that we at the Clinical Studies Division are completely convinced of the importance of the development of personal monitors, especially those in our own field of competence, and that we anticipate that our exposure chambers may well turn out to be the ultimate proving grounds for the personal monitors developed by our engineers and bioengineers, and for those monitors developed by other parts of EPA and other Agencies.

We are under no illusions concerning the scope and difficulty of the problems of development of personal monitoring equipment and the techniques involved in their use. We know that taking on this additional task will put further strain on our already critical staffing and space problems. Nevertheless, we intend to do our part and to do it to the very best of our ability.

We welcome this opportunity to play a role in what we feel is one of the major developments in environmental control of this time period. We also recognize the value of this symposium, and we appreciate the contribution it can make to this important human effort. We pledge our support and collaboration to the development of personal monitors for pollutant exposures and health effects measurement.

We look forward to taking part in this symposium, and we hope that all of you enjoy the symposium and the Carolina setting in which we are meeting.

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Role of the EPA Environmental Monitoring and Support Laboratory in the Development of Personal Exposure Monitors

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INTRODUCTION

Among other programs, the EPA Environmental Monitoring and Support Laboratory (EMSL) at Research Triangle Park (RTP), N.C., has organizational responsibility for evaluating and selecting air pollution monitoring instruments for use in studies required by the Clean Air Act as amended in 1977. In this capacity, EMSL recommends to the Administrator monitoring instruments for EPA designation, analytical techniques, and instrument performance specifications, in addition to conducting the air monitoring equivalency program. The EMSL/RTP also develops total monitoring systems and is responsible for the development and operation of the air pollution monitoring quality assurance program. Along with the EMSL/Las Vegas, the EMSL/RTP is currently applying its expertise in these areas to study designs using personal air monitors for human exposure assessment.

EXPOSURE MONITORING

The EMSL/RTP has responsibility within the EPA for the air pollution monitoring studies performed jointly with the Health Effects Research Laboratory/RTP health studies on human subjects exposed to both ambient and chamber-controlled concentrations of air contaminants. These air quality data and health data are analyzed by EPA biostatisticians to determine the degree of association, if any, of the measured health effects with the air quality data. Examples of two studies currently underway are measuring the effects of CO intrusion into vehicles and the effects of short-term exposures to high levels of NO_2.

We recognize that the ambient exposure levels monitored at a single fixed location may not be representative of the total exposure of residents in the study areas. To obtain a better definition of the spatial variability of pollution within the study community and the variations of exposure received by the subjects, a combination of fixed monitoring stations, mobile monitoring stations, and personal exposure monitors can be used to give a better estimate. The personal monitors used in these studies are tested by EMSL/RTP for interferences, accuracy, precision, temperature stability, etc. The results of the personal exposure monitoring data collection can be analyzed to test the hypothesis that the fixed-station data represent the average community exposure concentrations within a specified concentration bound and level of confidence. If the variations in exposure are significant, the biostatisticians can relate the measured variability of exposure to the health data by statistical techniques.

At the present time, the state-of-the-art personal exposure monitors have been developed primarily for occupational exposures to high levels of pollutants. We in EMSL see a need for increased development of personal exposure monitors for the lower ambient levels to which the general public is exposed.

In summary, I hope that this conference will improve communication between personal monitor users and personal monitor manufacturers and stimulate progress in their development as reliable instruments for human exposure studies. We anticipate that personal monitors will be used with increasing frequency as research monitoring tools for studies of health implications of air pollution and for relationships of different monitoring strategies.

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Personal Air Quality Monitors: Uses in Studies of Human Exposure

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I would like to explain very briefly how this conference fits into EPA's R&D Program. The Office of Research and Development (ORD), is one of the six main offices of the EPA. The other offices are often called the program offices, and are responsible for carrying out EPA's legislative mandate in areas such as air, water, noise, radiation, pesticides, solid waste, and toxic substances. These offices express their needs for research to ORD, which is then expected to find a way to answer those needs. This conference is one way we have chosen to address the need expressed in many different ways recently, by groups both inside and outside EPA, for methods of measuring human exposure directly.

In the last 2 years alone, four major groups have specifically requested action on the development and use of personal air quality monitors to measure day-to-day human exposure to air pollutants.

The National Academy of Sciences, in a 1977 report entitled Enviromental Monitoring, said: "We recommend that EPA coordinate and support a program to foster the development of small, quiet, sensitive, and accurate personal air quality monitors for use in conjunction with other methods of measuring human exposure to ambient air quality" (1). In 1977 the Second Task Force on Research Needs in Environmental Health Sciences recommended that: "...research is needed on the application of promising instrumental approaches to the development of personal monitors which, through use of micro-electronic components and small pollutant sensors, could be used to monitor individuals within populations of interest" (2).

EPA's own task force, the Standing Air Monitoring Work Group, charged with recommending an Agency-wide 5-year monitoring strategy, stated: "As a concluding observation, SAMWG believes that EPA should take a more active research role in determining the usefulness of personal air pollution samplers to measure the exposure dose to representative individuals" (3). And, a congressional committee in April of 1978 authorized a large increase in appropriations for studying effects of criteria pollutants, stating that: "...the Agency needs to improve the data base relating actual personal exposures to monitored ambient air pollution levels in order to increase the reliability of epidemiological studies. This should be done by development of personal dosimeters..." (4).

The last major conference on personal air quality monitors was held 3 1/2 years ago at Brookhaven National Laboratory. There, many possible technologies were ranked according to their probability of payoff within a few years, and a national R&D program of about $1.5 million a year for 5 years was recommended (5).

Such a program has not materialized to date, but some activity is taking place. For example, the Environmental Sciences Research Laboratory here in Research Triangle Park, N.C., has a project to develop a portable monitor for organics. This project will be further described later in this conference. This same laboratory supported a feasibility study (6) for personal monitors several years ago, and is now working on a monitor for respirable particles and gases, which will be described in the paper by Dr. Robert Shaw and Mr. Robert Stevens. A second ORD laboratory, the Health Effects Research Laboratory, has a briefcase-sized monitor for SO_2, CO, and NO_2 that it has developed over the past 2 years and may use in epidemiology studies. A third ORD laboratory, the Environmental Monitoring and Support Laboratory in Research Triangle Park, has used a commercially available CO dosimeter in a congressionally mandated study (7) of CO intrusion into sustained-use vehicles such as buses, taxis, and police vehicles. This will be described further in the talk by Dr. Richard Ziskind. Also, a fourth ORD laboratory, the Environmental Monitoring and Support Laboratory in Las Vegas, is administering an interagency agreement with the National Bureau of Standards (NBS) to develop one or more personal monitors for a pollutant or pollutants yet unnamed. Dr. Jimmie Hodgeson from NBS is here to give more information on NBS experiences with personal monitors.* Thus, I believe we are seeing the first stages of an effort that may lead to far more detailed knowledge of human exposure than we dreamed of 5 years ago.

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*Editor's Note: A copy of Dr. Hodgeson's symposium paper was not available at the time of printing and thus does not appear in these Proceedings.

For this effort to continue, however, even at a level far below the major national commitment called for by the Brookhaven workshop, it is necessary to keep its benefits clearly in mind. What are the benefits of a balanced program of development, evaluation, and use of personal monitors? I can see the following six major uses:

1) More detailed knowledge of individual, day-to-day exposure. Obtaining this knowledge requires that a large sample of people within a community be equipped with personal monitors and keep records of their activities. Together with fixed-station measurements, traffic and commuting records, and other personal activity models, the monitoring results will eventually allow estimates to be made of the frequency distribution of exposures for the entire community.

2) Identification of high-risk subpopulations and quantification of their exposures. The exposures at the high end of the frequency distribution are the controlling factors in determining the adequacy of our standards. The more precise our knowledge of the exposures of the sensitive portion of the population, the more precisely we can set our standards, avoiding both unnecessary economic impact if the standard is too stringent, and inadequate protection of human health if it is too weak.

3) Measurement of exposures during episodes. Although it is generally accepted that certain infamous air pollution episodes have cost scores or even thousands of lives (or at least they have hastened deaths that were imminent), no actual measurements have been made of individual exposures during episodes. To effectively measure exposures during episodes, which last only 3 or 4 days, it would be necessary to have a team of trained volunteers and the means of supplying them with monitors within a day of the beginning of the episode.

4) Validation of diffusion models and activity pattern models. Use of personal monitors in the field can provide data from hundreds of spatially dispersed points, multiplying by many times the number of points available from fixed-station locations. The same data can be used to validate the models of personal behavior--including commuting, shopping, and recreational travel--that will be necessary to develop as part of our total exposure models.

5) Calibration of fixed-station readings. A very valuable contribution of personal monitor studies would be the establishment of a solid relation between the fixed-station readings in a community to the exposures of at least some population subgroups in that community. If this is possible, then it would be conceivable that fixed-station readings in other communities would

bear a similar relationship to exposure. This would allow estimates of exposure to be made for more cities than those in which personal monitor studies had been carried out, and would also open up the possibility of using historical records of fixed-station measurements to estimate past exposures of community groups. Since chronic respiratory diseases depend on exposures over a number of years, this information would be valuable to the epidemiologist.

6) Development of dose-response curves. All five of the above purposes can be achieved without any concurrent measures of effects; they are pure exposure studies. Such studies presuppose that the effects at various concentrations--the dose-response curves--have been adequately established by clinical or epidemiological studies, and have been documented in the criteria documents or other publications. Of course, for many pollutants, this is not the case. For those pollutants, full-scale epidemiological studies, utilizing personal monitors for measuring dosages and lung-function tests or other medical end points for measuring responses, are necessary.

At present, the studies just outlined have yet to be carried out. As an illustration of the likely cost and time involved in carrying out such a study, I borrowed some equipment--the CO dosimeter (9000 series) of Energetics Science and the Dupont personal sampling pump--and measured my exposure while commuting from Reston, Va., to Washington, D.C., by bus for a period of 4 weeks last summer. This period proved sufficiently long to characterize my average exposure to within 10 percent. The instrument used is a small, light electrochemical device that can fit into a pocket or hook onto a belt. The Dupont pump is attached to the sensor by a flexible tube and can be inserted in a nearby pocket. A somewhat larger readout device can be placed in one's lap to allow minute-by-minute records to be kept, or it can be kept at the office or at home to give a total exposure reading. I preferred to keep a continuous record, which required leaving the dosimeter plugged in to the readout device while casting periodic glances (about every 5 minutes) at the edgemeter to document the changes that occurred in ambient concentrations. Figure 1 shows a typical exposure record obtained using this technique. You can see the high concentration in the bus as I boarded it, at a pick-up point where the engine had been idling for about 5 minutes. The concentration falls rapidly on the expressway (between 15 to 20 miles from D.C.), and then begins to rise as stop-and-go traffic is encountered near the city. It falls again while crossing the Potomac River, rises to a peak of about 30 to 35 ppm in the center of the city, and falls to 5 ppm or so as I walk to work. The smooth curve is the integrated exposure for the length of the trip, measured in ppm-hours. The total exposure was 35 ppm-hrs, over a total travel time of 53 minutes, which results in an average concentration for the trip of 40 ppm.

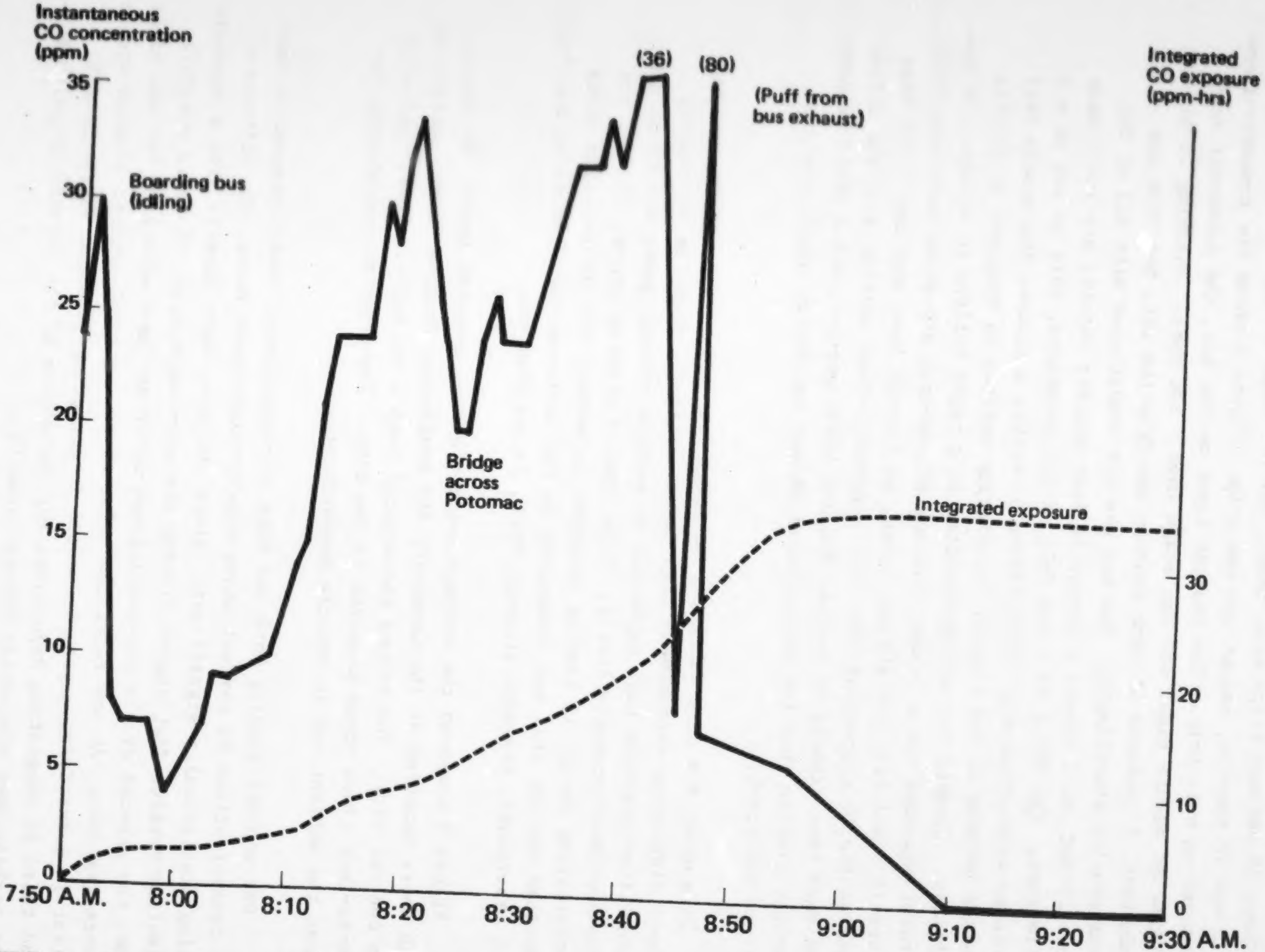

FIGURE 1. Exposure to carbon monoxide during commuting: sample trip.

About 30 one-way trips were taken, and the range of exposures varied between 5 and 35 ppm-hrs, except for one trip. Figure 2 shows the concentrations encountered on this trip. The instant I got on the bus, the dosimeter sent the edgemeter needle right off the scale (max = 100 ppm). Thinking it might be defective, I replaced it with another one from the kit, but this one behaved equally startlingly. The bus was air-conditioned with all of the windows closed, so I opened a window to test whether outside air would make a difference. (At 90° F on a bus full of hot commuters, this is not an act undertaken without careful deliberation.) Within a minute, the needle fell to values between 25 and 75 ppm, oscillating swiftly in response to traffic conditions. Closing the window resulted in a rapid buildup to values >100 ppm. The total exposure for a 1-hour trip was 65 ppm-hrs, and would have been >100 ppm-hrs if I had left the window closed, as I would have done had I not been measuring the CO concentrations. For a normal 8-hour working day, the driver would have been exposed to between 800 and 1,000 ppm-hrs, which would be considerably greater than the Occupational Safety and Health Administration limit of 400 ppm-hrs.

This exact bus (the identical vehicle) had been ridden the day before without displaying excessively high concentrations. Thus, an intriguing possibility--possible high exposures to vehicle exhaust gases due to maintenance problems--presents itself. This type of observation was in fact the precipitating factor in leading Congress to mandate the CO intrusion study described earlier that our laboratory in the Environmental Monitoring and Support Laboratory, Research Triangle Park, is carrying out.

Figure 3 compares the average concentrations measured inside the buses with those measured at the Community Air Monitoring Program (CAMP) station in the central city. The values encountered inside the vehicles were typically two-to-four times those measured in the city. There was no correlation between the ambient and in-vehicle measurements.

One unusual finding here was that air-conditioned buses appeared to have CO concentrations 60 percent above nonair-conditioned buses, the difference being statistically significant. Since the buses were diesels with a separate gasoline-powered jeep engine driving the air-conditioner, it seems possible that the exhaust of the air-conditioner motor may have accounted for the higher concentrations. At any rate, the value of the personal monitor in such studies--first in quantifying exposure, second in detecting possible unsafe levels, and third in suggesting hypotheses for the source of the in-vehicle pollution--has perhaps been adequately demonstrated (8).

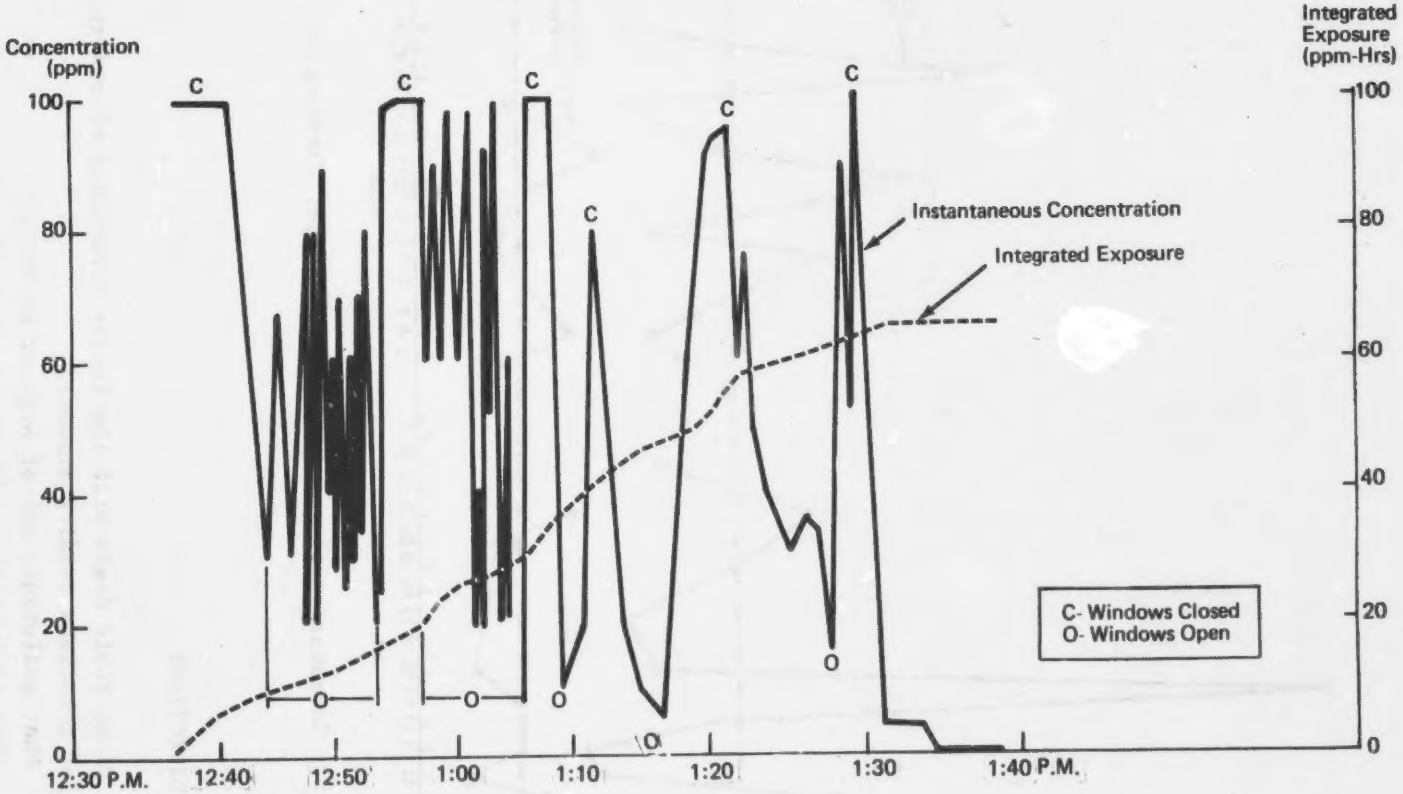

FIGURE 2. CO exposure during commuting: worst case (air-conditioned bus).

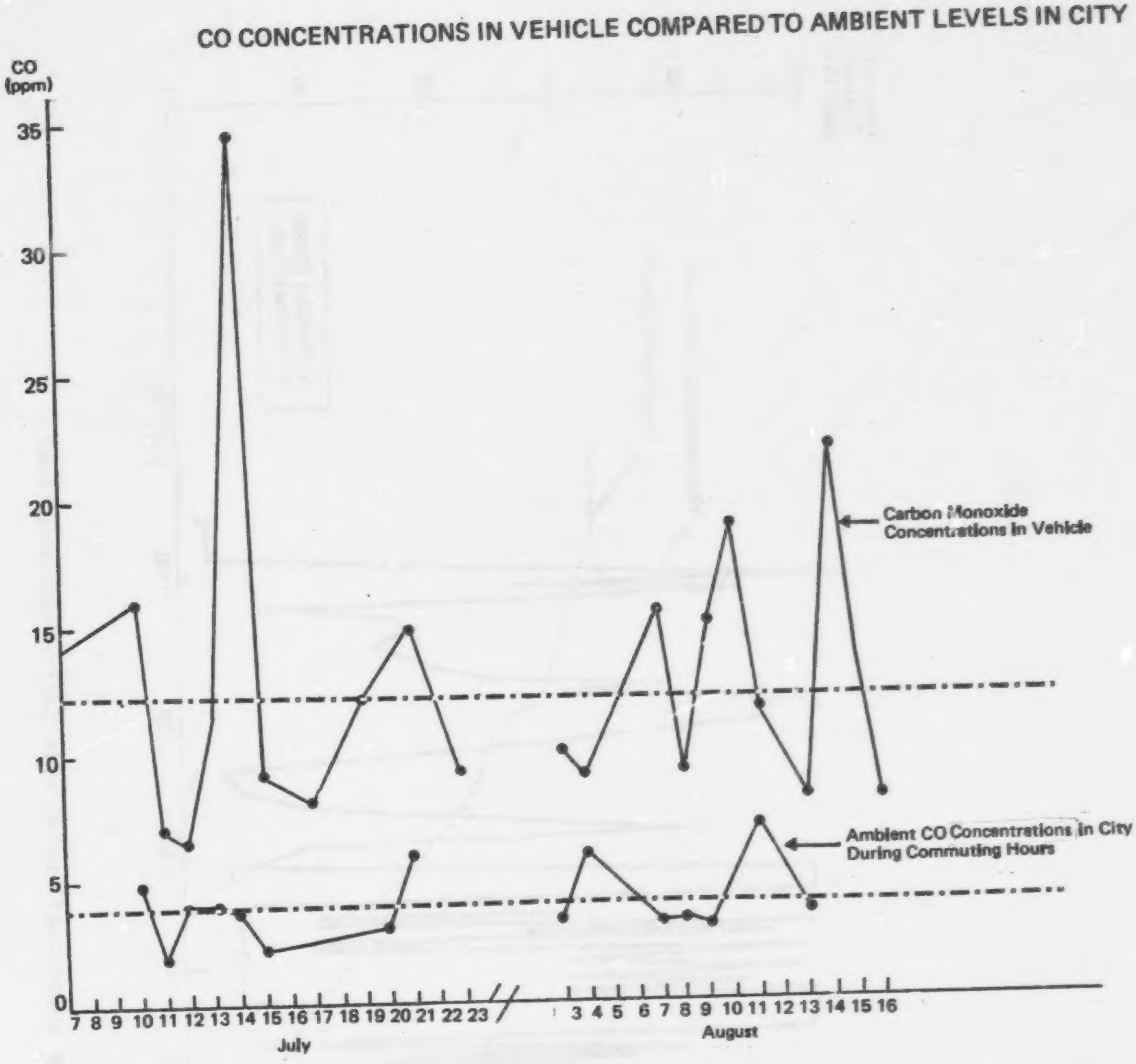

FIGURE 3. Commuter exposures to carbon monoxide: Washington, D.C., summer 1978.

FUTURE DIRECTIONS

My final topic deals with the future directions of research in this field. Four major questions require answers:

1) What pollutants are of highest priority?
2) What technologies are most promising?

3) What is the optimum balance among development, evaluation, and utilization of personal monitors?

4) How should this research be funded?

To the first question, I can bring responses recently solicited from EPA representatives of relevant program offices. The air program office has mentioned fine (inhalable) particulates as a high priority. We are in the midst of preparing for a possible standard on inhalable particulates, with a decision to be made in the early 1980's. A monitor capable of being deployed in fairly large numbers to establish dose-response curves and exposures to sulfates, nitrates, trace metals, and other components of the total respirable particulate load, would be highly desirable. Both the air office and the Office of Toxic Substances would also favor a monitor capable of collecting organics for later analysis in the laboratory. The extent of nonworkplace exposure to organics and to carcinogenic vapors is only hazily comprehended as yet. Other air pollutants of high priority to EPA will be discussed at the Tuesday evening workshop.

I will not attempt an answer to the second question: "What technologies are most promising?" It will be the major topic of our workshop session Tuesday evening and of the summary panel discussion Wednesday afternoon to which all are invited to attend.

The question as to what is the optimum balance between development and evaluation of personal monitors and their utilization in exposure studies may be partially attacked in the following manner: since the seven criteria pollutants have already had their health effects quantified, relatively inexpensive pure exposure studies--involving no concurrent health effects measurements and utilizing the most reliable commercially available instruments--should be of high priority. These studies will have the immediate benefit of providing the first reliable estimates of the exposures of an entire community population to a given criteria pollutant. This far more detailed knowledge of the population at risk could allow more efficient protective measures to be taken. Of course, a necessary prerequisite to such pure exposure studies would be the rigorous evaluation by EPA laboratories of the commercial instruments.

On the other hand, the development of new instruments must look beyond the criteria pollutants to the problems of the future--in particular, the toxic organics and fine particulates. This is not to say that development of instrumentation for SO_2, NO_2, ozone, and CO should not be supported; only that limited resources will require hard choices to be made.

This brings me to the final question--also called the bottom line--the question of funding. I have for several years advanced the thesis that in the absence of a mass market for personal monitors, the Federal government must support their development. At the same time, I felt that it could be to industry's advantage to fund development, since the more precise knowledge of exposures would allow fine-tuning ambient standards, with a probable reduction of economic inefficiency associated with too-stringent standards. A paper published by the National Academy of Sciences in 1977 called for an industry/government coalition on a development program (9).

Now, as a representative of government, I would make the same appeal--that we work together on developing and using the methods for determining more exactly our day-to-day exposure to air pollutants. I am very much heartened by the excellent response of the industry to this symposium, and I am certain we have a stimulating 3 days ahead of us.

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Discussion

NADER: John Nader, EPA, Research Triangle Park. I would gather concerning these personal monitors that they will be switched on and off as one enters from, say, environmental exposure outdoors to any kind of exposure indoors. Is this correct?

WALLACE: In the particular case that I was talking about, the monitor had enough range so that it was sensitive to both the concentrations that I was meeting on the bus and in the office. So, I left it on in the office for the first few days until I was determining that my exposure there was so low that it added essentially nothing to my exposure in the community. After that, I used the time to charge up the battery.

NADER: But the intent of personal monitors for environmental exposure would be to separate the exposure outside from the exposure inside; is that true?

WALLACE: I think it would be valuable to be able to make that separation. On the other hand, there may be cases in which it is far cheaper to collect something over the full 24-hour day, say, and send it off to the laboratory to look at.

In that case, you would only get an integrated exposure, and you won't be able to differentiate. But the cost benefit may make that worthwhile in some cases.

NADER: Doesn't that raise a question on the validity of the data so far as CO is concerned? For example, you might get considerable CO exposure indoors under smoking conditions, and this would affect your data?

It would give you the true fact of exposure. But as to attributing that exposure to outdoor levels, of course, that would be flexible.

WALLACE: Presumably one could get around that if, in the case you mentioned, we had a cheaper way of getting the total integrated exposure. For statistical purposes, we could equip a large number of people with monitors with the analysis done the cheaper way, and then equip a smaller statistical sample for continuous exposure such that we could differentiate the exposures due to various components of the data.

MAGE: Dr. West?

WEST: Phil West of Louisiana State University. I think John has already raised part of the question. Was there much smoking in the bus when you measured these levels that we are talking about so far?

WALLACE: In this case there was no smoking.

JOSEPHSON: Julian Josephson, Associate Editor, Environmental Science and Technology Magazine (ES&T). Do you believe that the source of the CO was the gasoline-powered air conditioning rather than the diesel engine of the bus, or is this not really determined?

WALLACE: It is not determined. But I have talked to people at the Department of Transportation, and they tell me that diesels do not put out much CO and that gasoline engines do, and that their guess was that it was the air conditioning. They also point out that these were older buses and that most newer buses operate the air conditioner off the same power plant--the diesel power plant. So, this particular problem may be seen less often in newer buses.

JOSEPHSON: You are talking about the famous Reston commuter bus--right?

WALLACE: That is right. They have about 70 buses. They are all diesels, circa 1955, and they have over 700,000 miles on them.

DOCKERY: Doug Dockery, Harvard School of Public Health.

What are the policy implications if we go out and do personal monitoring and find that personal exposures are not related at all to what the outside environment is actually telling us they are, and then we relate that back to health effects? What is EPA going to do about setting standards and changing their policy?

WALLACE: That is a very serious policy question about the indoor aspect of exposures. Many people feel that it has fallen through the crack with EPA doing outdoors, OSHA doing the workplace, and indoors and inside vehicles being not quite covered by any group.

The Need for Personal Air Pollution Exposure Monitors and Applications in Energy Development

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There has been much research in the past few years devoted to air pollutant transport and chemistry. These efforts provide a much better basis for relating ambient pollution levels to sources. Knowledge of the relation between ambient air pollution levels and individual or population exposure, however, is still very limited. People move around, spend most of their time indoors, and are exposed to pollutants from smoking, faulty auto exhaust systems, gas ranges, the workplace, and other sources. Even in air pollution epidemiology, where medical surveillance may be extensive, exposures are too often estimated from fixed monitoring stations serving neighborhoods or whole communities.

In investigating health-damage functions for use in comparing the health implications of various energy alternatives, our group concluded that the weakest link in determining such damage from air pollution is the accuracy of quantitative estimation of individual or population exposures to pollutants.

In 1975 we convened a workshop of health and instrumentation specialists to consider the role of personal pollution exposure monitors in air pollution health effects studies, and to assess research needs in this field.

Two early conclusions of the workshop were that "the importance of population exposure estimates in air pollution epidemiology makes it imperative that future epidemiological studies include exposure estimates more representative of what people actually breathe," and that "the use of individual air pollution monitors is a necessary factor in the design or performance of definitive studies of the health effects of air pollution" (2,3).

The Brookhaven workshop produced a first-order ranking, according to promise of ultimate performance, of a number of the candidate instrumentation technologies. These rankings, shown in Table 1, reflect a loose consensus of the participants at the time of the workshop.

For each technology, the workshop developed a first-order estimate of the research needs.

It seemed advisable to support development work on several of the more promising technologies in parallel before concentrating on a smaller number for further development.

Since the workshop, the Department of Energy has funded several projects aimed at developing personal exposure monitors.

Recently, Brookhaven was asked to organize and chair a working group to assess industrial hygiene needs for coal conversion and oil-shale industries, with an eye to the possible expansion of an instrumentation program already underway. A preliminary report of this working group has been issued (5). This has given us an opportunity to review the rather considerable advances in instrumentation made over the last 3 years.

Coal conversion plants will emit conventional combustion products (particulates, SO_2, NO_x) from the boilers needed to supply process heat to the conversion units. On an energy-produced basis, these pollutants are emitted at much lower levels than from coal-electric power plants. Conversion processes, however, involve the production of much more hazardous materials. These include heterocyclic compounds and reduced sulfur compounds. Facilities are designed to prevent the escape of these materials, but exposure of workers (particularly maintenance workers) must be considered. Since full-scale plants have not yet been built, the potential extent of public exposure--either routinely or in accident situations--cannot be well defined. Some surveillance among the public, at least during the start-up and early operation of such plants, seems warranted. Gammage et al. have pointed out the gap between the sophisticated analytic tools used in the laboratory to characterize pollutants from synfuels operations and the crude techniques available for measuring polycyclic materials in the field (1).

Among the range of heterocyclic compounds, the question of what specifically to monitor is especially important for field monitoring of population exposure. The need to develop one or more indices is important. Use of indices was strongly recommended by an interagency-supported investigation on health and safety guidelines for coal gasification (4).

TABLE 1

Tentative Ranking Developed by Participants in the Brookhaven Workshop on Individual Air Pollution Monitors of Candidate Gas- and Particle-Sensing Instrumentation Techniques

(Performance criteria applied in the ranking were the development of a prototype device of lunch box size or less with annual support of $200,000/year or less. The rankings are not based on a full quantitative analysis and should be viewed only as a qualitative guideline.)

Probability of Payoff	Within <3 yr	Within 3 to 6 yr
Outstanding	Gas Methods[a]	
	Sorption Gel tape colorimetry Electrochemical cells Coulometric and amperometric devices Fluorescence devices (SO_2) Nondispersive spectroscopy (CO) Chemiluminescence (O_3, NO_x)	Sorption methods Colorimetry (tape based) Electrochemical cells Coulometric and amperometric devices Fluorescence devices (SO_2) Nondispersive spectroscopy (CO) Chemiluminescence (O_3, NO_x)
	Particle Methods[b]	
	Virtual impactor (M, $2D$, C) Filters (M, $\sim N$, $\sim D$, C) Diffusion batteries with filters ($C(D)$) β meter (M)	Virtual impactor (M, $2D$, C) Filters (M, $\sim N$, $\sim D$, C) Diffusion batteries with filters ($C(D)$) Optical scattering (N, D) β meter (M)
Good	Gas Methods	
	Microwave devices (CO)	Electronic solid state devices Nondispersive spectroscopy (gases other than CO) Piezoelectric gas sensors Microwave devices (CO) Gas chromatography
	Particle Methods	
	Diffusion battery with condensation nuclei counter (N, D)	Virtual impactor (M, $>2D$, C) Diffusion battery with condensation nuclei counter (N, D) Piezoelectric mass balance (M, $\sim N$, $\sim D$) Optical scattering ($\sim N$, D)
Fair to poor	Gas Methods	
	Gas chromatography Cryogenic sampling Electronic solid state devices Nondispersive spectroscopy (gases other than CO) Piezoelectric gas sensors Microwave devices (gases other than CO)	Cryogenic sampling Bioluminescent methods Optoacoustic methods Microwave devices (gases other than CO)
	Particle Methods[c]	
	Piezoelectric mass balance (M) Optical scattering ($\sim N$, D)	

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[a] When the classification depends on the gas of interest, this has been indicated in parentheses. Techniques which were discussed but which the group did not feel qualified to evaluate included fluid-immersed solid state sensors and gas-sensitive liquid crystals.

[b] M indicates device appropriate for measurement of total suspended particulate mass; N, for measurement of total number of particles; and D, for measurement of particle *size* distribution. $2D$ indicates that sizing into two categories such as $\geqslant 3$ μm and $\leqslant 3$ μm is possible. C indicates device appropriate for collecting samples of particles for chemical analysis, and $C(D)$, that chemical composition can be estimated for two or more separate ranges of particle size.

[c] Other candidate technologies considered but viewed as unsatisfactory or inappropriate for use in individual air pollution monitors included liquid impingers, centrifugal separation, conventional impactors, thermal precipitation, electrical mobility, and microwaves.

A single index may not be appropriate for all situations. Gasification and liquefaction have different characteristics, and even different exposure situations from the same plant may be best evaluated with different indices, due to variations in the mix of compounds in the pollutant stream. Identification of indicator compounds needs to consider both the chemical characteristics of the mix of compounds and their biological activities. A problem, especially difficult in personal samplers, is that PNA's are likely to be in aerosol form or in vapor form subject to condensation in the sampling train.

From our perspective, other recommendations for future efforts include:

1) Personal air pollution exposure monitors are an essential step in quantifying individual and population exposure for protection, epidemiology, and regulation.

2) Passive samplers offer a cheap and convenient tool. They should be exploited much more extensively in population studies. New substrates should be developed to expand the diversity of measurable compounds.

3) Passive monitors are inadequate to fulfill the full promise and need from personal exposure monitoring. Development and demonstration of active devices which can sample and record short-time exposures are important.

4) Samplers must be field-tested under various conditions of interferences, temperature, pressure, humidity, etc.

5) Personal monitoring of particulate exposure is an area of great need, but it does not seem ripe for exploitation. Areas where continued support seem warranted are: a) improving efficiency of collection; b) improving extraction efficiency and separation techniques; c) chemical specification; d) in situ separation of soluble and insoluble particulates.

CONCLUSIONS

Regulatory decisions on air pollution control--which involve direct and indirect costs of billions of dollars--are being made without adequate knowledge of the health impacts of air pollution. The weakest link in the studies of health effects is our knowledge of individual exposures. The importance of population exposure estimates makes it imperative that future studies include exposure estimates more representative of what people actually breathe.

Personal air pollution exposure monitors that are easily carried or worn are essential for the design or performance of all definitive studies of the health effects of air pollution. Such monitors also have prevention and regulatory uses in public and occupational situations.

Given the enormous costs of air pollution control and regulation and the considerable uncertainties in our present understanding of the health impacts of air pollution, a coordinated national program of support for the development and use of personal air pollution exposure monitoring instruments should be initiated without delay.

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Discussion

JOSEPHSON: Josephson, ES&T Magazine. Do you foresee that the present effort concerning the anti-inflation fight might have an adverse effect on the development of this instrumentation and coordinating activity that you advocate?

HAMILTON: No; I frankly don't think so, because from what my job is and from the point of view of inflation, one is thinking in terms of controls, as they apply to plants 10 or 15 years from now.

I am not quite sure what those capital requirements for those plants are--whether the capital has to be on line for many years in advance or not.

But it seems to me that what we are talking about is a few millions of dollars. It is so insignificant when I compare it to the gross national product of the United States that I can say that it would have actually no relationship whatsoever.

The only thing is this: if we did have a better understanding of what the dose effect relations were, we would feel more confident as to whether or not we were justified in spending these large sums on control. Let me just say this: we are going to spend these large sums on control anyway. We are committed to this even in the present state of uncertainty. For example, the health effects of something such as sulfate are uncertain. Although we can't say with 95 percent certainty that sulfate is causing an increased mortality, certainly we can say this with 60 percent certainty, and under these circumstances, we have to go ahead with these expensive controls. What I am saying is that from the point of view of public policy, this tiny investment in air pollution and personal monitors is kind of a dreary thing for many people. I don't think they like to support the idea of developing measuring instruments. I think this is one of the reasons why it possibly hasn't been supported.

ZISKIND: Richard Ziskind from Science Applications. You mentioned the problem for the need to develop indices if one wants to deal with the events called commercial processes. What are the limitations right now as you see them in developing such indices? Are there monitoring problems or identification of levels or substance identification that should be of concern?

HAMILTON: I frankly don't think there are any problems. A more likely problem is apt to be in having to develop a good personal monitor. I am sure we can raffle off a number of possible indices. I have already mentioned one of them.

What we need is a monitor for a simple heterocyclic compound characteristic of what might come out of the process. I feel that the problem lies in the development of the actual good personal instrument rather than in the choice of the indices.

But again, that is the sort of subject I feel one could develop in the process of discussion.

CHASE: Paul Chase of Beckman Instruments. You mentioned the DOE is sponsoring the development of some instruments. Is that only your shop, or did I misunderstand what you said? How about a portable gas chromatograph?

HAMILTON: The pocket-sized gas chromatograph? I am not sure who is actually doing that. However, it is almost at the commercial stage. But I am not sure who that would be.

I think that Beckman would be very interested in commercializing it.

Current NIOSH Research on Passive Monitors

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I would like to take this opportunity to describe to you the work that is currently being undertaken by the National Institute for Occupational Safety and Health (NIOSH) and its contractors in the area of passive monitors. We are studying not only points of current interest, but also future applications of passive personal monitors.

For lack of any other, I would like to offer the following definition of passive personal monitors. (Please keep in mind that this definition is dependent upon the interests and responsibilities of NIOSH in the area of personal exposure monitoring.) A passive personal monitor is a device worn on an individual for the purpose of measuring--without the use of an active flow mover--personal exposure. The key aspects of the definition are threefold: 1) the device is worn on the individual--preferably within the breathing zone; 2) the device uses no active flow mover, such as the typical pump that is necessary with the various solid sorbent tubes; and 3) the device measures personal exposure. These characteristics are the opposite of those of an area monitor.

There are several advantages to passive monitors. This type of monitor--interchangeably referred to as a badge--is small, lightweight, and easily worn by any individual. This is an advantage over personal sampling pumps, which can weigh up to 2 pounds each. The monitors are free of liquid content, which makes them preferable to impingers and bubblers. The subsequent chemical analysis of passive monitors is generally similar to existing methods. The badges, however, are not without disadvantages. Whether the badge uses the

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principle of diffusion or permeation through a membrane, there is an extra factor (not necessary with the use of sorbent tubes and pumps), which is either the diffusion coefficient of the species through air, or the permeation constant of the species through the membrane material used in the badge. This constant must be known for each compound. In addition, there is evidence--even with sorbent tubes--that high humidity alters the adsorption of various solvents. In the case of sorbent tubes, desiccant tubes may sometimes be used preceeding the sorbent tube. It is not yet apparent what can be done to correct for high humidity effects in passive monitors.

The emphasis of NIOSH's current research with passive monitors centers on the passive organic monitors. Most of the studies involve the Gasbadge, marketed by Abcor Development Corporation, and the Organic Vapor Monitor, marketed by the Minnesota Mining and Manufacturing Company. One study also includes the MiniMonitor, marketed by the Reiszner Environmental and Analytical Labs, Inc.

The Abcor Gasbadge is 8 cm long, 5.7 cm wide, and 2 cm deep. It weighs approximately 40 g and consists of seven parts: the sliding cover; the front plate of the badge, which has a 4.4 cm x 3 cm opening to allow diffusion of gases; a protective screen; a draft shield; an open grid that defines the diffusion geometry; the collection element; and the back plate of the badge. One unique feature of the Gasbadge is that the newer-designed case allows for placement of a second collection element which can be used to take a second sample or can be used as a field blank. The Gasbadge is reusable by replacing the collection element.

The 3M Organic Vapor Monitor is a circular badge that is 10.2 cm long (including the clip), 4.4 cm wide at its widest point, and 1.2 cm deep. The sampling opening is circular with a 3-cm diameter. This badge weighs 13.5 g. During sampling, the unit consists of six pieces: the outer rim; the draft shield, which is held in place by the outer rim; an open grid that defines the diffusion geometry; the collection element; and the solid back piece of the monitor. The sixth piece is the clip for attachment to the person. The 3M monitor is the only passive monitor that we are currently using that allows for in situ sample elution. The 3M badge is not reusable.

The MiniMonitor, which was developed by Philip West at Louisiana State University, is also a circular badge. Its diameter is 5.0 cm, it is 0.625 cm thick, and it weighs 35 g. There are two features unique to the MiniMonitor: the badge works on 1) the principle of permeation of contaminant gases and vapors through a membrane; and 2) adsorption of the pollutant(s) onto approximately 1.35 g of PCB activated charcoal. This is free-flowing, as opposed to the collection elements of the two previously mentioned badges. The MiniMonitor case is reusable by introducing a fresh supply of charcoal.

The most basic ongoing research with the passive monitors is an evaluation of the passive monitors that is being conducted at the Utah Biomedical Test Laboratories under contract to NIOSH. The purpose of this study is to establish the reliability and the working characteristics of the Gasbadge, the Organic Vapor Monitor, and the MiniMonitor. This effort consists of eight tests that are designed to study various properties of the badges. All of the tests are being conducted in a specially designed and constructed exposure chamber with accurate control and monitoring of temperature, humidity, concentration of the contaminant being used in the study, face velocity, and exposure time. Even though independent checks are being constantly run on the concentration--i.e., via GC, PID, or other calibrated instruments--in all of the tests in this study, charcoal tubes are being used in side-by-side sampling with the badges. The charcoal tube sampling is used as a reference because the method represents the state-of-the-art in sampling for organic vapors and is the best "primary standard" available.

In the first test with the badges and the tubes, we will consider the precision of the measurement with the badges, and the comparability of the badges with the charcoal tubes. Under conditions of constant temperature, humidity, face velocity, and time, the badges and charcoal tubes will be simultaneously exposed in 12 tests. The 12 tests are comprised of four contaminants at three concentration levels each. The contaminants to be used in this study are vinyl chloride, acetone, toluene, and a mixture of n-hexane and acetone.

The effects of storage on the sample accuracy will be studied. In this test, one set of monitors and charcoal tubes will be exposed to methylene chloride. A matching set of monitors and charcoal tubes will be exposed to toluene. Monitors and tubes from each exposure will be divided into three groups to be analyzed at three times--within 1 day of exposure, on the 7th day following exposure, and on the 14th day following exposure.

Perhaps the most difficult test is that which will consider maximum and minimum levels of quantitation and the capacity of the monitors. These tests have been designed to determine over what concentration range and exposure times the sampling and analytical methods for the monitors will provide a precision and accuracy of ± 25 percent of the "true" value for 95 percent of the samples.

A fourth study will look at the effects of face velocity on the badges. The face velocities will be varied from essentially stagnant conditions to 400 fpm. Orientation of the badges will also be studied, with the contaminant approaching from the front, side, and back of the badges in three separate tests.

Effects of temperature from 0° to 40° C and humidity from 10 to 80 percent relative humidity will be studied in two different series of tests.

Out-gasing or back-diffusion from the badges could be a serious shortcoming of the monitors. It is possible that back-diffusion could occur in a situation where a worker would be exposed to a very high concentration of some contaminant and then move to an area of no exposure. Back-diffusion could occur, due to the concentration gradient, depending upon how tenaciously the contaminant is adsorbed to the collection element. To study this phenomenon, three tests have been designed that look at nonconstant concentration exposure and continually varying concentrations.

The final test in this contract involves exposing the monitors to a complex mixture, such as refined petroleum or coal tar products, and comparing the badge results to the charcoal tubes.

The Division of Surveillance, Hazard Evaluation, and Field Studies of NIOSH is undertaking an effort to accumulate comparative field sampling data between the Gasbadge, the Organic Vapor Monitor, and charcoal tubes. This effort will result in a report later this year that contains 500 points of comparison data between passive monitors and charcoal tubes--all from field applications.

We are also engaged in research that involves possible future applications of passive organic monitors. Our Organic Methods Development Section is attempting to develop a passive monitor for aldehydes. Their approach is based on a derivative formation.

Another of the more complex problems with the passive monitors is the question of saturation. How do we know when the collection elements have reached their capacities for adsorption of contaminants? In the laboratory--under controllable conditions--it is easy to determine the point of saturation. But what happens in the field if the exposure of a worker is being measured and the passive monitor saturates? To address this question, we are undertaking an effort to look at two-stage passive monitors. In this study, we determine the capacity of a collection element by plotting exposure time versus percent recovery. Saturation of the collection element is indicated by the drop off in the curve from the theoretical 100 percent recovery, and the capacity of the element can be calculated from this exposure time.

What we hope to be able to detect is the breakthrough of the contaminant through the first collection element and to determine the validity of the sample. When the first collection element is saturated, there will be a concentration gradient to the back of the badge in the direction of the second collection element. There will probably also be a less dramatic gradient between the first collection element and the ambient air. Because of these developing gradients, we hope to be able to detect the contaminant on the second element after the badge has been exposed up to its saturation point. This will be a great aid in using the passive monitor in the field.

Another type of passive monitor is a personal atmospheric gas sampler with a critical orifice which was developed through an interagency agreement between NIOSH and the Naval Research Laboratory. This whole air sampler uses the leak through a critical orifice to meter the air flow into an evacuated container. The critical orifice admits air at a constant rate up to one-half atmospheric pressure. An 8-hour sample can be taken. For analysis, the sampler is connected to a gas chromatograph, through a gas sampling loop interface. The pressure of the gas sample is measured using a manometer placed in the gas sampling loop. The advantages of the whole air sampler--besides being small, lightweight, portable, and requiring no personal pump--are that the sample taken never undergoes a phase change, the sample is never handled, and there are never breakthrough and desorption problems. One disadvantage to the whole air sampler is that it does not provide an enrichment step, and, therefore, sample analysis requires sensitive analytical instrumentation. Substances with low-level standards may not be sampled in this fashion.

Passive monitors are currently available for NO_x, SO_2, Hg, and the organic solvents. The U.S. Army Environmental Hygiene Agency has been working on a passive monitor for ammonia. Soon, independent companies will make available passive monitors for NH_3, SO_2, HCl, and NO_x, as well as marketing uniquely designed passive monitors for organic solvent vapors.

NIOSH is planning to look further into passive monitor use by testing different solid sorbents as the collection element and perhaps looking into some electrochemical applications of passive monitors. As far as their application to ambient personal monitoring goes, the present state-of-the-art passive monitor has some major drawbacks: 1) the monitors generally lack specificity (a drawback of some other sampling techniques as well); and

2) the detection limits of the monitors--at the low end of the scale--may not meet the needs of ambient sampling. While it is true that collection on the element is an enrichment step, it could take quite a long time to accumulate a detectable sample from ambient air. With certain new products that are coming out, and as the technology allows us to develop more effective monitors, passive monitoring will be useful in the ambient situation.

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Discussion

WALLACE: Lance Wallace, EPA. Is that cold air sampler going into commercial development?

WOEBKENBERG: MDA markets it.

WEST: Phil West, Louisiana State University. I can make a comment, which is not a question. One is that the permeation-type badge does handle liquids. In fact, they use that on a chlorine badge that we have just developed. In that case, incidentally, it is specific for chlorine if the ozone does not interfere.

I might also mention that so far humidity has no effect on the badges that we have developed based on permeation.

WOEBKENBERG: Some of the studies that we have run have shown a humidity effect. The data have not been worked up yet, but we have seen a minor humidity effect.

But that is true about the liquids. There are some passive monitors that will be available. In fact, there are some that are already available that do use liquids as the collection element. Some of them will be talked about today. And some of them are not yet ready to be spoken of. But there are some liquids also available.

THOMAS: Charles Thomas. You mentioned that some of the monitors were specific and some were not. If they aren't specific, how do you get around the problem of determining what the lowest level of exposure should be if the collection efficiencies vary from gas to gas?

WOEBKENBERG: Well, I said that the monitors are not specific. Generally, I mean in the case of the organic vapor monitors. The charcoal collection elements will trap organic vapors, and in that case, they are not specific.

In order to resolve the question of specificity, then you have to rely on your analytical method to do that for you. However, in the case of some of the passive monitors--as Dr. West mentioned, they have one for chlorine and 3M has one for mercury--there are certain monitors that are specific. But in the case of nonspecificity, they have to rely on the analytical method to resolve that problem for you.

THOMAS: Isn't it a collection device and not a monitor?

WOEBKENBERG: That is true; yes.

Electrochemical Methods for Development of Personal Exposure Monitors

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Becton Dickinson and Company
Elmsford, New York

INTRODUCTION

Recent social and legal requirements have given great impetus for the development of personal exposure monitors for a variety of gaseous pollutants. Since the exposure of a normally active individual is not accurately represented by a fixed-site monitor, there is a need for personal monitors in order to measure the actual human exposures.

The application of our electrochemical sensing method has resulted in a variety of practical monitors for the measurements of CO in ambient air. This established technique has been applied to personal dosimetry for CO in the workplace environment. An evaluation of this device demonstrates that the performance characteristics of the larger fixed-site instruments can be achieved in a compact, lightweight personal exposure monitor.

This instrument approach to dosimetry overcomes many of the historical disadvantages of integrated dosage measurement. The CO Dosimeter, Ecolyzer 9000 Series, enables accurate measurement of dosages over short-time intervals and correlation of exposure and physical activity.

A PERSONAL MONITOR FOR CARBON MONOXIDE

The success of the electrochemical method for the measurement of carbon monoxide in the workplace environment is well known. In the sensor, carbon

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monoxide is electro-oxidized to carbon dioxide at a potentiostatically controlled platinum electrode in aqueous electrolyte and follows the reaction

$$CO + H_2O \rightarrow CO_2 + 2\ H^+ + 2\ e^-$$

The signal produced upon exposure of the sensor to an air mixture is proportional to the partial pressure of carbon monoxide in the gas which is analyzed.

This current flows between the sensing and counter electrode, and the reaction at the counter electrode is

$$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$$

therefore yielding an overall cell reaction of

$$2\ CO + O_2 \rightarrow 2\ CO_2$$

This sensing method has been developed and adapted for personal monitoring. In order to accomplish this task, it was required that the sensor be miniaturized and designed for ruggedness. Further, accurate measurement of the TWA while worn by the worker performing routine activities necessitated that the instrument performance be insensitive to both orientation and vibration.

The gas is introduced into the sensor (shown schematically in Figure 1) by means of a sampling pump. The sensor is a miniaturized three-electrode electrochemical cell. The Teflon-bonded diffusion electrodes are in contact with the aqueous electrolyte, which itself is suspended in an immovable matrix. The matrix allows the sensor to be operated in any special orientation.

The sensor is interfaced with an instrument system, which is described schematically in Figure 2. The compact system design has a volume of approximately 300 cc and a weight of 0.43 kg (12 oz). The critical working elements consist of pneumatics, sensor and electronics for power control, amplification, and storage. During operation, an external pump draws a sample of ambient air through the pneumatic system at a constant flow rate. The sensor continuously monitors the concentration of carbon monoxide in the sampled air stream. This concentration-related signal is amplified and converted into digital pulses for storage in a digital circuit. The battery pack is capable of supplying power in excess of 2 years of dosimeter operation. A flow-adjust valve allows for fine control of the sample flow rate. The prefilter removes particulates

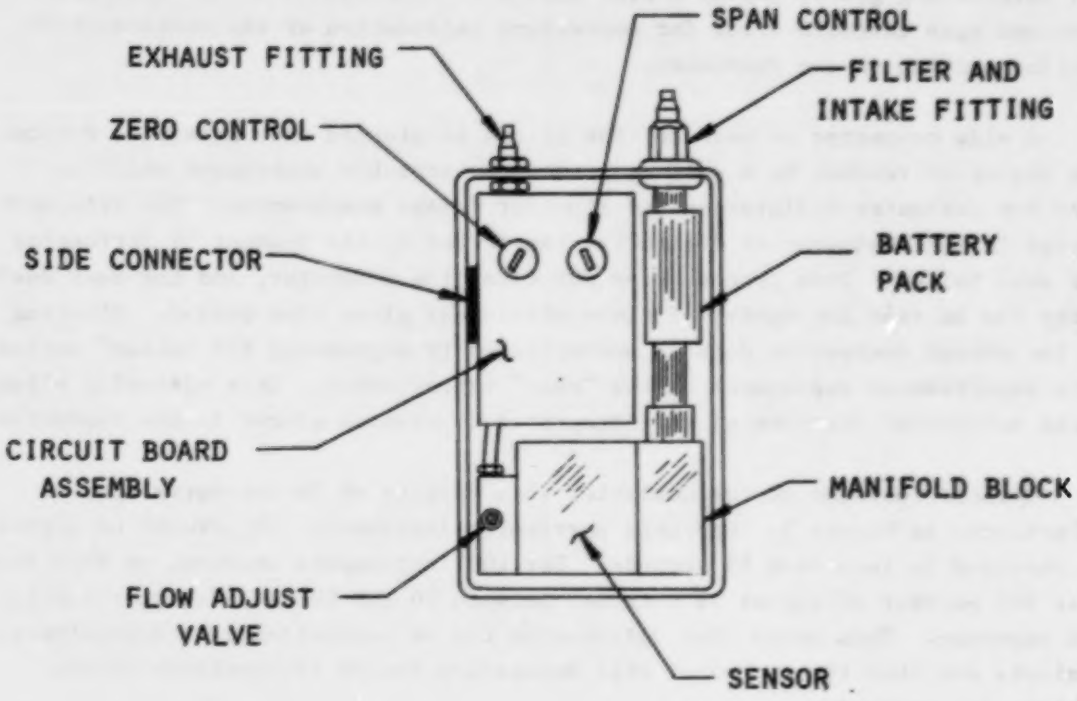

SPAN CONTROL
EXHAUST FITTING
FILTER AND INTAKE FITTING
ZERO CONTROL
SIDE CONNECTOR
BATTERY PACK
CIRCUIT BOARD ASSEMBLY
MANIFOLD BLOCK
FLOW ADJUST VALVE
SENSOR

FIGURE 1. Dosimeter schematic.

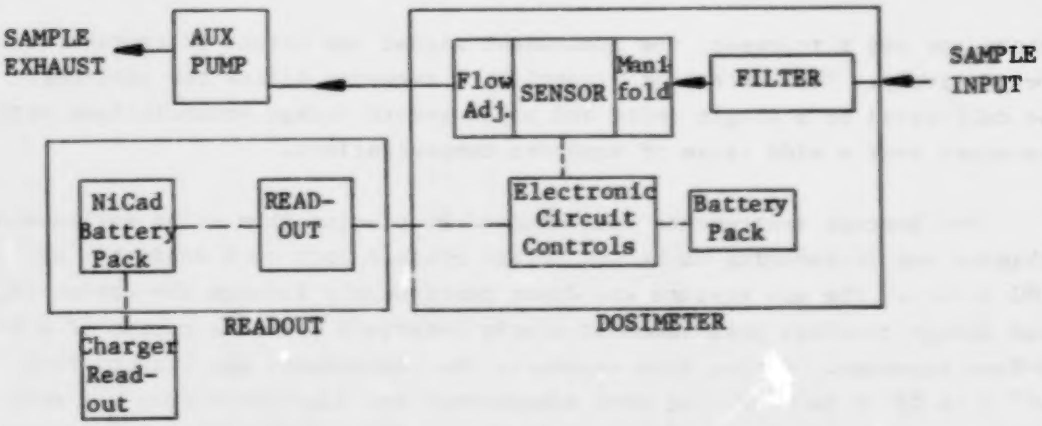

SAMPLE EXHAUST
AUX PUMP
Flow Adj.
SENSOR
Manifold
FILTER
SAMPLE INPUT
NiCad Battery Pack
READ-OUT
Electronic Circuit Controls
Battery Pack
READOUT
DOSIMETER
Charger Read-out

FIGURE 2. Instrument system schematic.

and interfering gases, giving a high degree of specificity to the analysis. Zero and span controls allow for convenient calibration of the continuous CO monitor section of the dosimeter.

A side connector is made so that it can be plugged into a readout device. The dosimeter readout is a self-contained rechargeable instrument which is used for dosimeter calibration and also for dosage measurement. The data collected in the dosimeter is digitally transferred to the readout by depressing the read button. This process does not clear the dosimeter, and the same dosimeter can be read any number of times within any given time period. Clearing of the stored dosimetric data is accomplished by depressing the "clear" button with simultaneous depression of the "read" button twice. This virtually eliminates accidental clearing of the integrated CO reading stored in the dosimeter.

Typical response of the dosimeter to a variety of CO concentrations is illustrated in Figure 3. For this particular instrument, 98 percent of signal is obtained in less than 45 seconds. For 100 instruments studied, we have found that 100 percent of signal is obtained between 20 and 60 seconds after initial gas exposure. This means that calibration can be accomplished in approximately 1 minute and that the dosimeter will accurately record fluctuations in the ambient concentration.

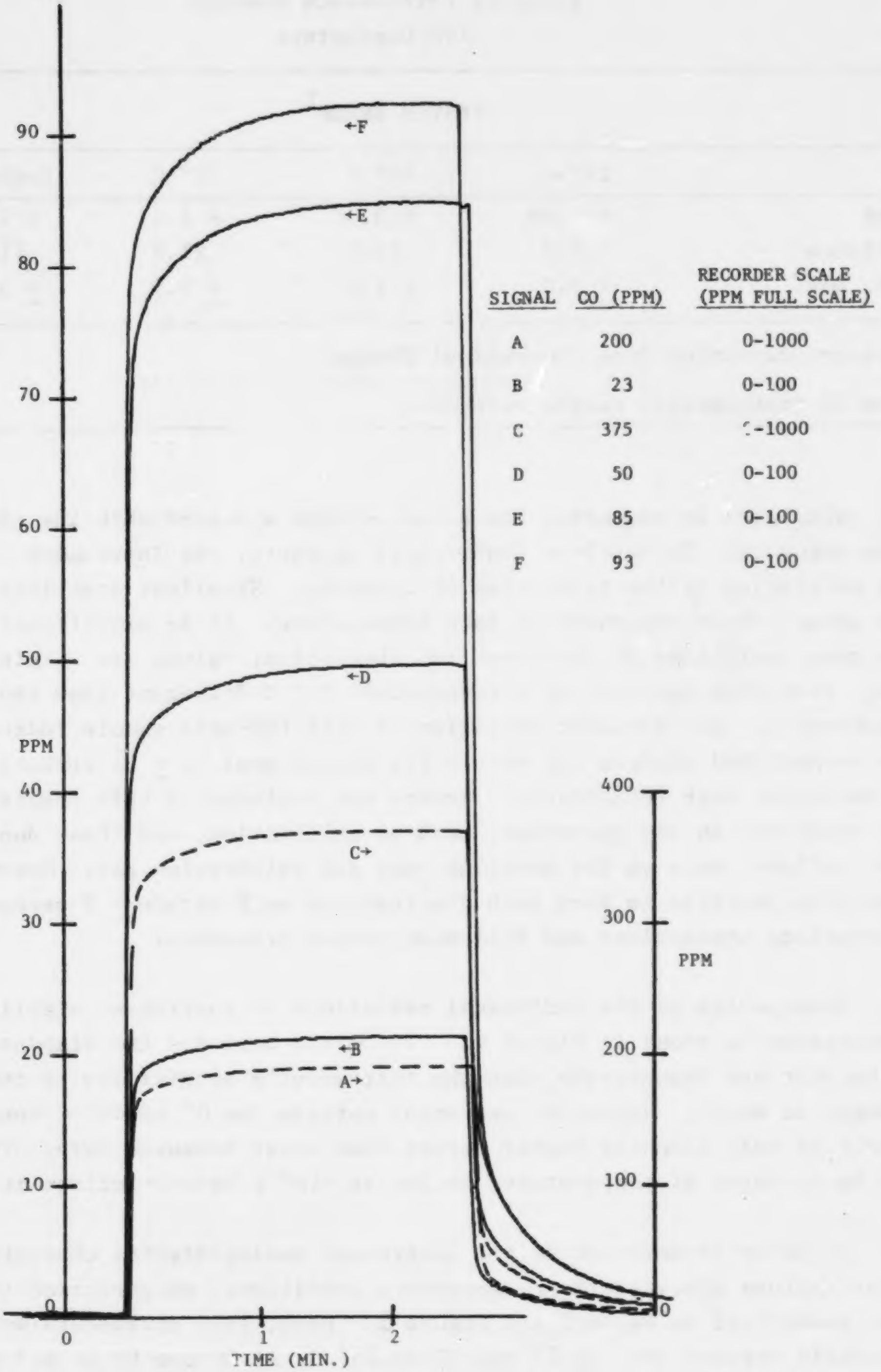
For this instrument, the magnitude of the response can be expressed by the equation

$$\text{ppm} = 0.98x - 0.38$$

where ppm and x represent the instrument signal and actual CO concentration, respectively. This excellent linearity of response allows the instrument to be calibrated at a single point and still record dosage accumulations with accuracy over a wide range of exposure concentrations.

One hundred instruments were studied by placing them in an environmental chamber and introducing an 84 ppm CO/air mixture into each dosimeter at 100 cc/min. The gas mixture was drawn continuously through the dosimeter, and dosage readings were taken at hourly intervals over the course of a 6- to 8-hour exposure. During this exposure, the temperature was changed from 40° C to 22° C to 0° C. At each temperature the instrument span and zero were recorded. Analysis of this data revealed the instrument performance characteristics at three temperatures and over a long time exposure.

The data is summarized in Table 1 for 100 instruments. The system error



SIGNAL	CO (PPM)	RECORDER SCALE (PPM FULL SCALE)
A	200	0-1000
B	23	0-100
C	375	0-1000
D	50	0-100
E	85	0-100
F	93	0-100

FIGURE 3. Dosimeter response versus time at various CO concentrations.

TABLE 1
Ecolyzer Performance Summary
100 Dosimeters

	SYSTEM ERROR[1]			
	22° C	40° C	0° C	Combined[2]
Mean	+ 0.46	+ 0.96	+ 2.5	+ 2.10
Variance	9.0	24.2	27.8	11.6
Std. Dev.	± 3.0	± 4.9	± 5.3	± 3.41

[1] Percent deviation from theoretical dosage

[2] For 25 instruments, random selection

was calculated by comparing the actual dosage measured with the theoretical dose exposure. To obtain a theoretical exposure, the instrument span at 22° C was multiplied by the total time of exposure. Excellent stability is found for these 1-hour exposures at each temperature. It is significant to note that the mean deviations of the dose from theoretical values are within ± 2.5 percent, even when operated at a temperature 20° C different from the calibration temperature. The standard deviation of this 100-unit sample indicates that the accumulated dosages are within the design goal of ± 15 percent error with an extremely high reliability. Errors not included in this analysis, however, are those due to the operation, such as calibration, and those due to equipment failure, such as the sampling pump and calibration gas. However, it should be possible to keep such fluctuations well within ± 5 percent by using appropriate precautions and following proper procedure.

Examination of the individual variations of instrument stability with temperature is shown in Figure 4. The error bars are two standard deviation units wide and demonstrate that the instrument's sensitivity to temperature changes is small. Operation can occur outside the 0° to 40° C range and will result in only slightly higher errors than those measured here. The sensor can be operated at temperatures as low as -10° F before failure is observed.

In order to demonstrate the instrument analog/digital characteristics under various concentration/temperature conditions, we performed the experiment summarized in Table 2 and Figure 5. Here, five dosimeters were simultaneously exposed to: 1) 85 ppm CO at 24° C, 2) 50 ppm CO at 24° C, 3) a temperature change to 40° C with 50 ppm CO exposure, 4) continued 50 ppm

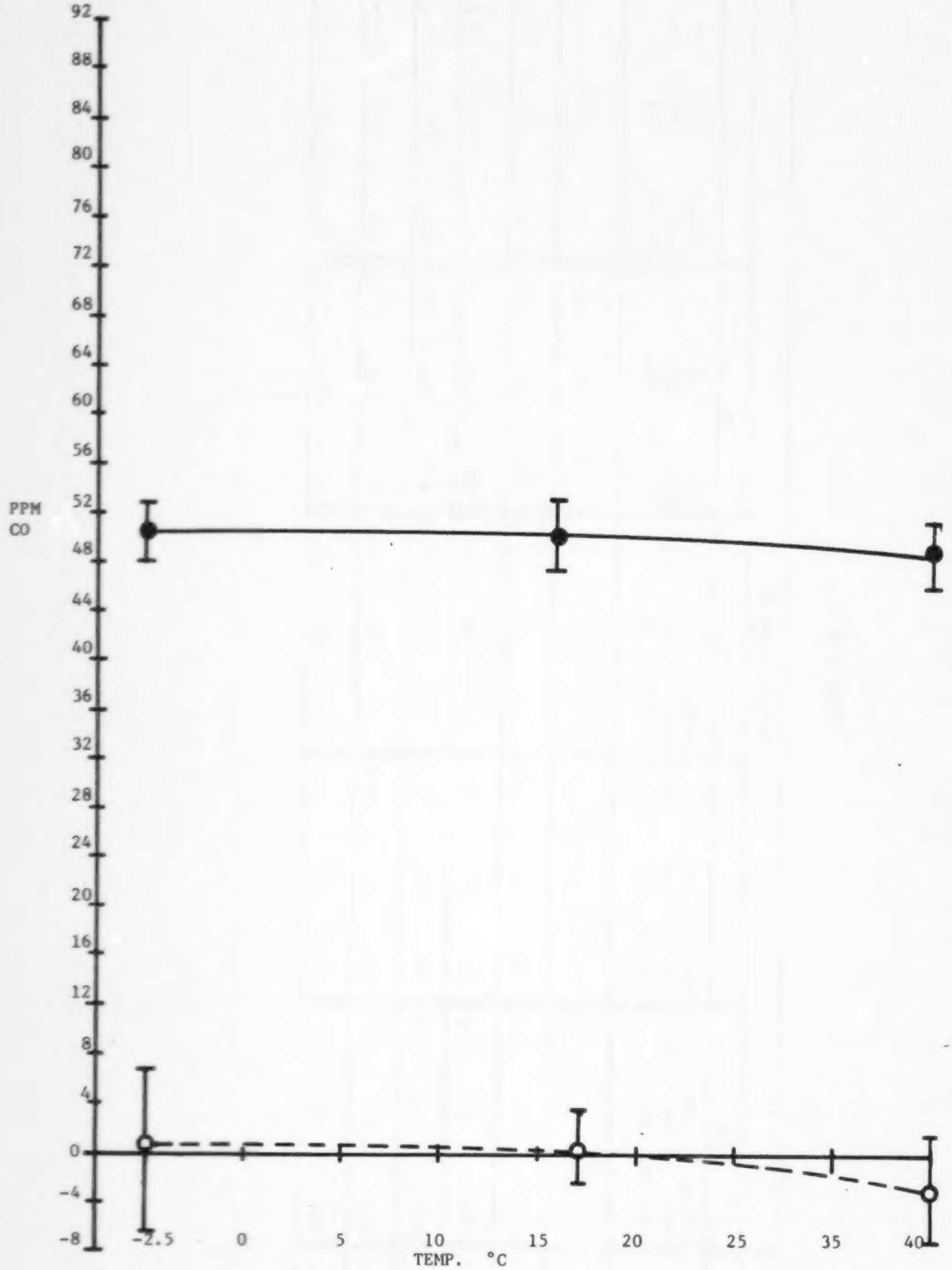


FIGURE 4. Dosimeter zero and span versus temperature.

TABLE 2

DATA POINT	DOSIMETER NUMBER														
	1179			1091			1206			1291			1191		
	THEOR. DOSE PPM HRS.	ACT. PPM HRS	% DEV	THEOR. DOSE PPM HRS.	ACT. PPM HRS	% DEV.	THEOR. DOSE PPM HRS	ACT. PPM HRS	% DEV.	THEOR. DOSE PPM HRS.	ACT. PPM HRS	% DEV.	THEOR. DOSE PPM HRS.	ACT. PPM HRS	% DEV.
A	0	--		0	---	---	0	---	---	0	---	---	0	---	---
B	85	84	-1.2	86	85	-1.2	87	88	-1.2	89	86	-3.3	90	90	0
C	142	140	-1.4	142	140	-1.4	143	140	-2.1	144	137	-4.9	145	144	-0.7
D	196	190	-3.2	197	190	-3.6	197	189	-4.1	198	186	-6.1	199	196	-1.5
E	246	236	-4.1	247	235	-4.9	247	234	-5.3	248	231	-6.9	249	245	-1.6
F	335	320	-4.5	336	318	-5.4	338	315	-6.8	339	314	-7.4	341	333	-2.5

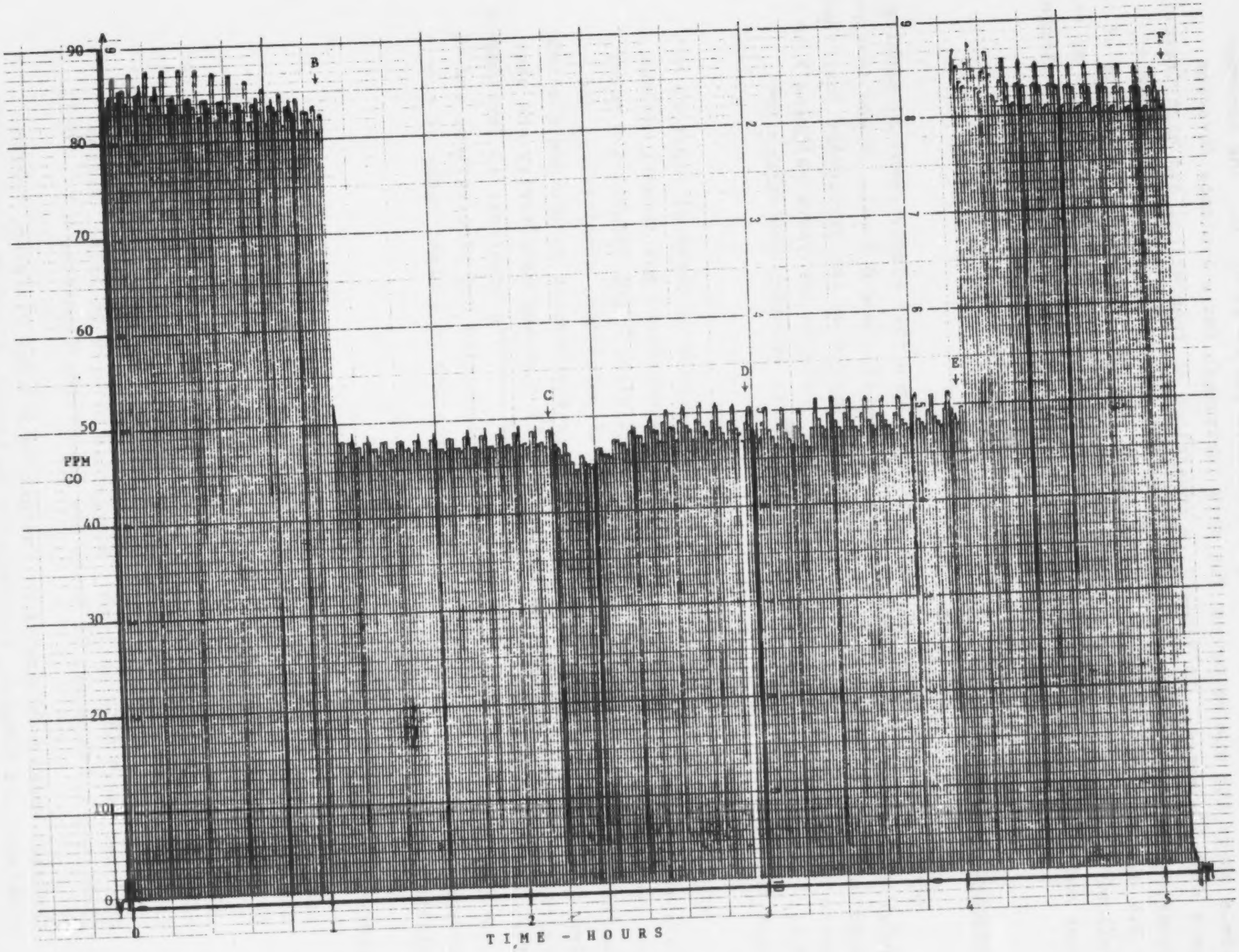


FIGURE 5. Dosimeter analog output versus time.

exposure, 5) 85 ppm CO at 40° C, and 6) zero ppm CO at 40° C. The recorder trace shows the analog output for each instrument for a 1-minute duration once each 5 minutes. In Table 2, a comparison of theoretical and experimental dosages (digital outputs) is summarized; the dosimeters had a mean error of - 3.4 percent ± 2.1 percent. One observes that the instrument is capable of following dosages accurately with a single calibration at the initiation of the test and in the presence of 20° C temperature changes and concentration changes.

PERSONNEL MONITORING

Other personnel monitors that are based upon this electrochemical sensing method are available for hydrazines (1,2), NO_2 (3), and H_2S (4). These instruments have not been miniaturized to the same degree as the previously described carbon monoxide dosimeter; however, they are portable analyzers weighing 5 to 10 kg. Further, other devices are possible with existing technology for gases such as NO and SO_2.

The future holds great promise for development of personal monitors of miniature size using Energetics Science electrochemical gas sensing methods. This technique offers the advantages of small size, light weight, low power, stability over long sampling periods, ease of operation, sensitivity, and ruggedness. Primary areas which will require development to provide electrochemical personal monitors are related to: 1) improved sensitivity and stability to widen the application range without reducing accuracy; 2) development of auxiliary instrument systems related to pneumatics and electronics; and 3) improved specificity for expanding the application to a wider range of contaminated environmental samples.

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2. Stetter, J.R., Tellefsen, K.A., Saunders, R.A., DeCorpo, J.J. Electrochemical Determination of Hydrazine, Methyl- and 1,1-dimethylhydrazine in Air. Talanta (in press).

3. Ecolyzer Model 6632 Analyzer, Energetics Science Division, Becton Dickinson and Company, 85 Executive Boulevard, Elmsford, N.Y. 10523.

4. Ecolyzer Model 6430 Analyzer, Energetics Science Division, Becton Dickinson and Company, 85 Executive Boulevard, Elmsford, N.Y. 10523.

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Discussion

ZISKIND: Richard Ziskind of Science Applications. I wonder if you are concerned about electromagnetic interference with these devices, such as radio transmission--something like that?

STETTER: Yes. The circuitry is susceptible, and there are a lot of wires and things. We don't find high-frequency interference on most of our monitors because they have metal cases.

On these particular small ones, they have light plastic cases. And we found it necessary to coat the inside of the plastic case with a metallic coating which is grounded. We had one of these successfully tested at the Kennedy Space Center. And it shows indeed that the HF sensitivity is very low.

SPENGLER: John Spengler, Harvard School of Public Health. A couple of questions: one is about cell life, and two, have you ever actually field tested this alongside of an NDIR CO monitor? Because I am concerned about the highly fluctuating nature of real CO exposure.

STETTER: Early in the game, we compared the electrochemical technique and NDIR for CO measurement. We found that by and large our response times were much better because they have a lower purge rate for the larger cell. You can purge this cell very rapidly so you get a very good response characteristic. In terms of cell life, we warranted these kinds of cells for 6 months. And generally speaking, with proper care and normal ambient conditions where the relative humidity is, you know, 40 to 80 percent, you should get a lifetime in excess of a year.

SPENGLER: What is the cost of the cell and the unit?

STETTER: The instrumentation comes in a kit of five which gives you the readout and five dosimeters for about $3,000, give or take a little bit.

WILLIAMS: Marsha Williams. Do I understand that it was tested with flow rates, temperatures, and humidity checks like that at ambient levels which are more typical in the environment that EPA would like to monitor?

STETTER: There is a field test now; at least these devices have been and are actually being used in the field.

WILLIAMS: I don't mean field testing. I am talking about your sensitivity test to see how sensitive they are to flow rate.

STETTER: Right. In the laboratory, we of course did the flow rate study, which was easily accomplished.

WILLIAMS: Have you done any studies at low level concentrations to see whether or not there is a difference in effect?

STETTER: Yes. And there is no difference in effect because the response is linear. It is a percent of span. In other words, if you have 50 ppm and you drop 1 ppm or 1 percent of span where you measure 100 ppm at the same flow rate, you would get 98. That would be 2 percent of the signal. It is a percent span change with flow rate--that is the characteristic.

Now, we have done relative humidity at all three temperatures, at 0 to 100 percent. The only effect you get is dilution of your calibration gas. It is the only effect you can see, and there is no signal to monitor at all.

HODGESON: Jimmie Hodgeson, National Bureau of Standards. Can you give us any more details--is there an active relation between your electrical signal and electrical return in the amount of CO going through the sensor?

STETTER: Yes. There is a signal relationship. For example, if you went to higher flow rates, you can get higher currents--put more CO through it. So, in terms of more detail: yes, in effect.

SPENGLER: You didn't show any data on interferences. I know there are several with the Ecolyzer such as NO. And it is the same principle, I assume?

STETTER: Well, there is not an interference due to NO with a proper filter. The filter has scrubbers and adsorbents in it which take out NO, NO_2, SO_2, H_2S, and other electrochemically reactive gases. So, you get a high degree of specificity. Without the filter in place, you can get signals from other electrochemical reactive gases.

SPENGLER: Would that be a concern with personal monitoring as opposed to stationary monitoring?

STETTER: Yes.

Portable Ozone and Oxidant Monitors for Random Field Surveys

Gary P. Heitman and Richard L. Sederquist
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INTRODUCTION

Small, portable electrochemical instruments capable of measuring ozone (O_3) at the parts-per-billion (ppb) level are widely used in industry as safety monitors near ozone generators and ozone-producing processes, and in quality control of ozone-producing appliances such as photocopy machines and electronic air cleaners. Similar instruments, or measuring techniques, may be suitable for use in ambient air monitoring at remote locations, complementing the existing fixed-station network.

AVAILABLE INSTRUMENTATION

While the once-popular colorimetric potassium iodide (KI) analyzers are no longer manufactured, amperometric KI instruments are currently available in several convenient configurations. Similar in design to the well-known Mast Ozone Meter (Model 724-2), which was widely used for ambient air pollution studies prior to 1975, Mast Series 724 Oxidant Monitors utilize an electrochemical sensor with buffered 2 percent KI reagent. Details on the detection technique have been given by Mast and Saunders (4). Recent instruments, while retaining the original detection technique, offer several design improvements, including a signal amplifier which allows multiple-range direct readout, increased sensitivity at low O_3 levels, and zero/span adjustments. Reagent is supplied from a single reservoir with enough capacity for up to 30 days continuous operation. Two models are appropriate for ambient level

O_3 monitoring--Model 724-5, a.c. powered (see Figure 1), and Model 724-4, battery powered (see Figure 2). The battery-powered model was designed according to National Institute for Occupational Safety and Health (NIOSH) guidelines for construction and performance standards for compliance monitoring in the industrial environment (6) and will operate 20+ hours on a fully charged battery. Both instruments weigh less than 12 pounds and are easily transported.

PERFORMANCE, OPERATIONAL STABILITY

Although relatively low in cost and simple to maintain and operate, certain electrochemical monitors can exhibit exceptional performance.

A Mast amperometric KI oxidant monitor was evaluated against analyzers using chemiluminescent and ultraviolet absorption measurement methods in a field study at Los Angeles and St. Louis during 1970-1972 (3). Long-term calibration stability and general operational characteristics were compared. Results are shown in Tables 1 and 2.

More recently, a Model 724-5 monitor was evaluated by a project team at Harvey Mudd College, Claremont, Calif., for potential use as a commercial aviation O_3 monitor. The instrument was calibrated prior to shipment using the 1 percent neutral buffered potassium iodide (NBKI) procedure. After 30 days of continuous use at the college, the instrument's calibration was checked at the State of California Air Resources Board station at El Monte. The Air Resources Board (ARB) uses a Dasibi UV absorption monitor and a special three-meter ultraviolet instrument for comparison in calibration (11). The Mast monitor, Serial Number 2370, agreed with the ARB standards within six-tenths of 1 percent (0.6 percent) (11).

Parker (6) reported similar calibration stability in a study for NIOSH and also determined that neither changes in relative humidity (0 to 100 percent) or changes in ambient temperature (10° to 40° C) significantly affect the measuring efficiency of the Mast monitor. Other operational characteristics which make the Mast monitor suitable for field use are convenient size, quiet operation, low maintenance, and long-term unattended operation.

PERFORMANCE, ACCURACY IN O_3 MONITORING

Obviously, there must be some disadvantages in the use of an amperometric KI system. Photochemical oxidants have been traditionally defined

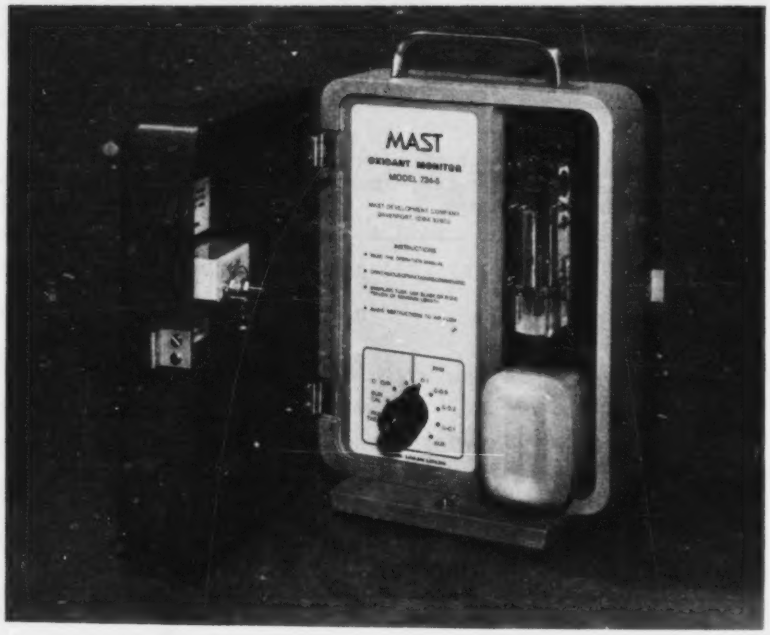
MAST
OXIDANT MONITOR
MODEL 724-5

FIGURE 1. Model 724-5 Oxidant Monitor, front door open. Oxidant measuring ranges are 0-0.1 to 0-1 ppm.

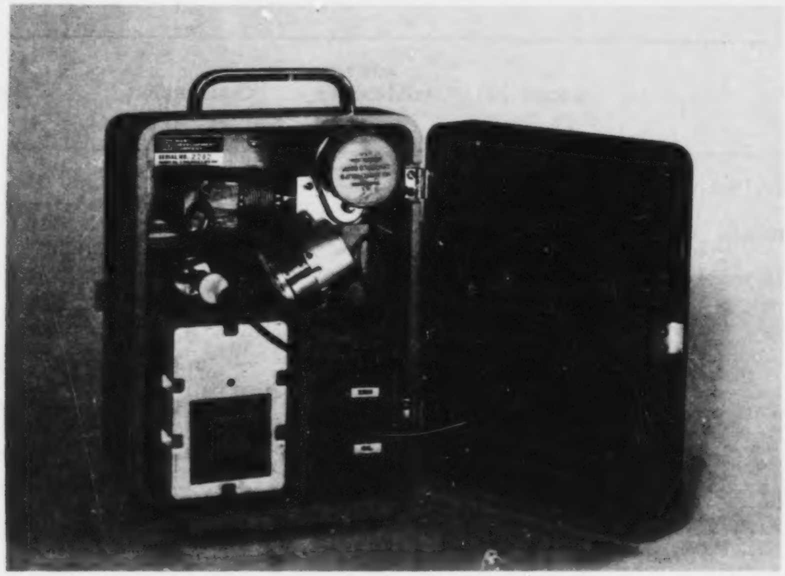

FIGURE 2. Rear view of Model 724-4 Oxidant Monitor. High-capacity lead acid battery powers monitor for 20+ hours.

TABLE 1

Long-Term Calibration Summary for O_3 and O_x Instruments [a]

Instrument	Pollutant	Number of calibration points	Minimum detectable concentration (ppm)	Average zero drift (ppm/day)	Average span drift (%/day)	Correlation coefficients
Bendix Env. Sci.	O_3	23	0.0066	0.0001	0.072	0.882
Bendix Process	O_3	105	0.0003	-0.0000	-0.128	0.998
RTI (Solid Phase)	O_3	52	0.0004	-0.0000	-0.074	0.992
Dasibi	O_3	21	0.0011	-0.0001	-1.749	0.967
Beckman	O_x	67	0.0122	-0.0001	0.592	0.963
Mast [b]	O_x	103	0.0003	0.0000	-0.129	0.993
Technicon	O_x	74	0.0118	-0.0004	-0.552	0.947

a. Reference 3
b. Mast O_x, Model 724-2

TABLE 2

General Operational Characteristics for O_3 and O_x Instruments [a]

	Number of days tested	Ambient monitoring time (%)	Calibration time (%)	Downtime (%)
Bendix Env. Sci. O_3	94	94.7	2.9	2.4
Bendix Process O_3	74	94.3	2.4	3.3
RTI (Solid Phase) O_3	185	94.1	2.7	3.2
Dasibi O_3	32	98.5	1.4	0.1
Mast O_x [b]	256	94.2	3.3	2.5
Technicon O_x	256	87.5	4.5	8.0
Beckman O_x	65	90.0	5.5	4.5

a. Reference 3
b. Mast O_x, Model 724-2

as substances which will oxidize a KI reagent, which responds to O_3 with nearly 100 percent efficiency, and to a lesser extent, to peroxyacetal nitrate (PAN) and hydrogen peroxide--all components of the photochemical oxidant mixture--and also to nitrogen dioxide (NO_2). Sulfur dioxide (SO_2) reacts negatively, reducing an oxidant-caused signal. The most important disadvantage of the amperometric KI system, therefore, is its nonspecificity. Sulfur dioxide is a major interferent because it reduces iodine formed in the KI reaction from contact with oxidant back to potassium iodide, producing a strong negative interference. A SO_2 filter (Model 725-30) is available for the Mast instrument. Consisting of glass fiber paper impregnated with chromium trioxide and sulfuric acid, as described by Saltzman (7), it has proven to be effective in over 7 years of field use and experimental evaluation (5,7). A potential disadvantage in the use of this filter is its ability to oxidize nitric oxide (NO) to NO_2, causing additional interference in O_3 determination. This may not present a problem, however, since O_3 and NO rarely coexist. Use of the filter would be disadvantageous in only a few areas (such as Los Angeles), where concentrations of NO are relatively high and those of SO_2 low (7).

The Mast monitor will also respond to approximately 12 percent of PAN present in a sample and to 9 percent of hydrogen peroxide (2). Since these compounds generally exist at low levels in ambient air, compared to ozone levels (1), interference potential is usually insignificant.

Assuming SO_2 is filtered or is not present, the major interferent to contend with is NO_2. The efficiency of the Mast monitor in measuring NO_2 is approximately 6 percent. The efficiency drops at high ozone levels. For instance, if an O_3 level of 0.25 ppm is being sampled concurrently with a 0.55-ppm level of NO_2, instrument response will be 0.28 ppm O_x (9), an error of only 5 percent.

In actual field use, an electrochemical KI oxidant method can show equivalent performance when compared with a chemiluminescent and UV photometric O_3 method. Wendt (10) reported that the California ARB compared, at three separate stations, a total oxidant analyzer (colorimetric KI), an ethylene chemiluminescent ozone monitor, and an ultraviolet photometric ozone monitor. The experimental results showed the total oxidant, ultraviolet photometric, and ethylene chemiluminescent monitoring methods to be equivalent over a range of 0 to 500 ppb at the three sites. Other recent comparisons also show, in general, small differences between KI oxidant data and ozone data, especially when instruments are standardized with the same calibration atmosphere and when appropriate corrections for major interferents are considered (1).

A MINIATURE SENSOR FOR PERSONAL EXPOSURE MONITORING

A miniature KI oxidant sensing device currently used in a Mast Brewer ozonesonde may be adaptable for use as a personal O_3 exposure monitor. Figure 3 shows the major components of a Mast bubbler/pump assembly, and the general dimensions.

Packaging, including electronics, readout, and housing, would produce a miniature monitor about the size of a cigar box weighing less than 1 pound. (See Figure 4.)

Table 3 gives estimated performance specifications. Other parameters have not been fully evaluated. (See Figures 5 and 6.)

The bubbler sensor is a small electrolytic cell which contains a few milliliters of KI reagent. A miniature pump forces ambient air continuously through the cell at a constant rate of 200 cc/min. The cathode is fine platinum gauze, and the anode is a silver wire. The arrangement of the cell is such that the bubbling action also provides the maximum possible flow of the solution through the cathode gauze. When a potential of 0.42 V is applied across the cathode and anode, it balances a spontaneous emf associated with the detector, and no current will flow unless free iodine is present. As the air containing O_x bubbles through the electrolyte, free iodine (I_2) is formed which contacts the cathode screen, through diffusion and the sensor bubbling

TABLE 3

Estimated Performance Specifications of Mast Miniature Bubbler [a]

PERFORMANCE PARAMETER	UNITS	OXIDANT
Range	ppm	0-0.5
Noise	ppm	0.005
Lower detectable limit	ppm	0.009
Zero drift, 8 hour	ppm	0.005
Span drift, 8 hour	ppm	0.005
Rise time, 90 percent	Minutes	5
Fall time, 90 percent	Minutes	2.5

[a] Tested on bromine permeation tube standard

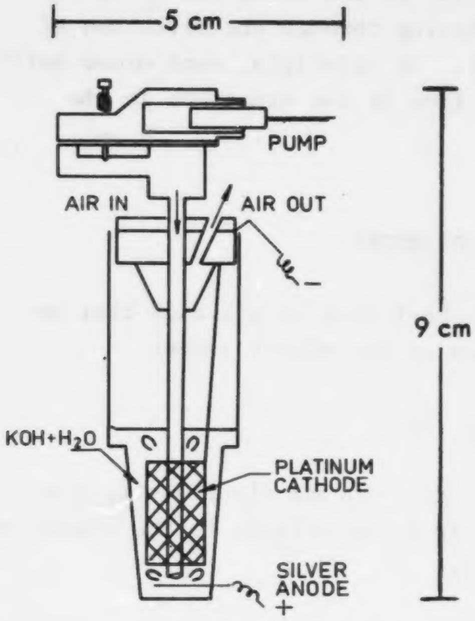
5 cm
9 cm
PUMP
AIR IN
AIR OUT
KOH+H2O
PLATINUM CATHODE
SILVER ANODE
+
−

FIGURE 3

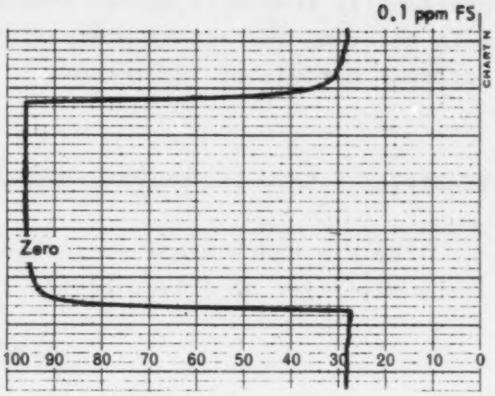

FIGURE 5

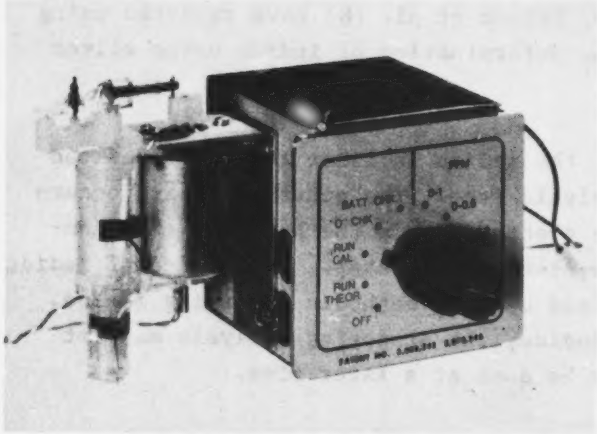
PPM
0-1
0-0.5
BATT CHK
"O" CHK
RUN CAL
RUN THEOR
OFF

FIGURE 4

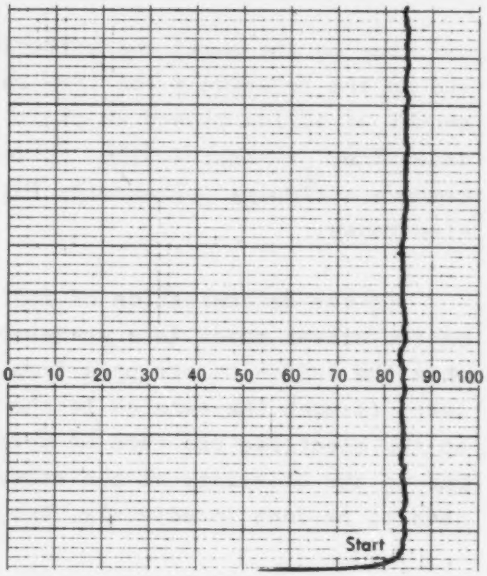

FIGURE 6

FIGURE 3. Miniature oxidant sensor.

FIGURE 4. Experimental bubbler-monitor weighs less than 16 oz.

FIGURE 5. Typical chart recording from oxidant bubbler. Bubbler is ranged for 0-.1 ppm O_x full scale. Chart speed is 5 cm/hr.

FIGURE 6. Chart shows Mast bubbler output over a 6-hour period. Oxidant source level is 0.084 ppm. Chart speed is 2 cm/hr.

action, and is reconverted to iodide ($2I^-$). At the anode the I_2 is reformed, but it is prevented from recirculating through the formation of practically insoluble silver iodide (AgI). In principle, each ozone molecule entering the sensor gives rise to a flow of two electrons in the external circuit of the sensor.

FEASIBILITY OF USING OXIDANT BUBBLER AS DOSIMETER

The electrochemical processes of the Mast bubbler are such that an insoluble layer of silver iodide is formed on the silver anode:

$$Ag + I^- - e \rightarrow AgI$$

As the silver iodide (AgI) is relatively inert to the electrolyte, the amount of iodide plated on the anode should be equivalent to the amount of oxidant which has passed through the cell.

Due to the small concentration of oxidant being sampled (less than 1 ppm) and to the relatively low flow rate of the pump (nominally 200 cc/min), the amount of iodide plated on the silver in light hours is too small to be determined gravimetrically. However, Perone et al. (8) have reported using cathode stripping voltammetry for the determination of iodide using silver electrodes.

In the determination of iodide, the iodide is first electro-deposited on the silver anode in a pre-electrolysis step. The actual analysis occurs when the iodide is stripped from the electrode. In the bubbler, the chemistry is much the same as in the pre-electrolysis step. The amount of iodide on the electrode can then be determined using a cathodic stripping method. Due to the stability of the silver iodide, the stripping analysis may not need to be done immediately, but may be done at a later time.

DISCUSSION

The EPA has suggested (1) that, ideally, O_3 should be measured at locations downwind from the source-intensive center-city area, if peak O_3 concentrations are to be recorded. Increased rural surveillance has also been suggested. Since concentrations of NO_x in an urban air mass decays rapidly as the air moves away from the city (1), nonspecific KI oxidant monitors may be suitable for this task. The cost-ratio for chemiluminescent O_3 or

UV photometric O_3 methods versus the amperometric KI (Mast) method is nearly five-to-one.

A miniature KI oxidant instrument, currently used for atmospheric O_3 research, may be useful as a personal exposure monitor, or, when used with a tethered radiosonde, a tool for tropospheric mixing and transport studies.

Amperometric KI oxidant monitors and sensors are rugged, small, low in cost, and exhibit excellent stability. These versatile instruments may prove useful in supplementing data collected at fixed-monitoring stations.

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Personal Sampler for Measurement of Ambient Levels of NO_2

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INTRODUCTION

The NO_2 sampler to be described is a "passive" device. The only driving force for the collection of molecules of the contaminant gas is the random motion of the molecules themselves. There are, therefore, no requirements for pumps, flow regulators, or batteries. Because of this, the devices can be made very lightweight, inexpensive, and maintenance-free. These characteristics make them ideally suitable for the purpose for which they were designed; i.e., the measurement of NO_2 in underground mines. Prototypes of this kind of sampler were reported by Palmes and Gunnison (4) in 1972 and published (5) in 1973. The subject device was published by Palmes et al. (6) in 1976, a publication which describes the NO_2 sampler both from the practical and theoretical standpoints (the reader is advised to consult this publication for details of construction, operation, and application to the workplace environment). An attempt will be made in this paper to describe the general features of the device and the theoretical background, as well as to demonstrate the applicability for monitoring NO_2 at the community and the industrial levels.

DESCRIPTION OF SAMPLER

The sampler consists of a 3/8-inch I.D. acrylic tube, approximately 3 inches long. One end of the tube is permanently closed with a close-fitting polyethylene cap, inside of which are three stainless steel screens coated with triethanolamine (TEA), which is an excellent absorbent for NO_2, as reported by Levaggi et al. (2) and by Blacker (1). During sampling, the other end of the tube is open to the environment to be sampled. Since the TEA maintains the NO_2 concentration at the closed end of the tube at or very near zero, a concentration gradient is set up between the open and closed ends of the tube. This causes a net flow of NO_2 from the environment to the TEA, where it is captured. For storage both before and after sampling, both ends of the sampler are capped. The complete sampler weighs approximately one-quarter ounce. The materials for the construction are inexpensive, and all of the components except the polyethylene caps are cleaned and reused. It is estimated that a technician could either prepare or analyze approximately 100 samplers in a working day.

THEORY

The quantity of NO_2 transferred by diffusion during an exposure can be calculated using Fick's First Law of Diffusion. This law states that if there is a concentration difference between the two ends of a diffusion barrier, there will be a flux of the gas species for which the concentration difference exists. This flux will increase linearly with the concentration gradient and with the cross-sectional area of the diffusion path, and will decrease linearly with the length of the diffusion path. The quantity of gas transferred by diffusion will also depend on the time of the diffusion flux. This can be expressed in the equation

$$Q_{NO_2} = D \frac{A}{L} ct$$

where Q_{NO_2} = quantity of NO_2 transferred during exposure (moles)

D = coefficient of diffusion of NO_2 in air (moles/cm^2)
A = cross-sectional area of tube (cm^2)
L = length of tube (cm)
c = concentration difference between open and closed end (moles/cm^3)
t = time of exposure (sec).

Thus, it is seen that the sampler depends on three constants, D, A, and L, and on two variables, c and t. Since for a particular tube the dimensions are known and the coefficient of diffusion can be estimated from values in the literature, when one measures the quantity of NO_2 trapped and knows the time of exposure, he/she can calculate the time-weighted average concentration.

SAMPLER PERFORMANCE

To determine the accuracy and precision of the samplers, it was necessary to set up known environments of NO_2 and to expose the samplers for definite times to these environments. Known concentrations were produced by diluting the output of an NO_2 permeation tube maintained at a constant temperature. The constants for the sampler described were:

$$D_{NO_2 \cdot Air} = 0.154\ cm^2/sec,$$

$$A = 0.71\ cm^2,$$

$$\text{and } L = 7.1\ cm.$$

Substitution of these constants and conversion to more conventional units gives the expression:

$$Q_{NO_2} = 2.3\ (ppm\ NO_2 \times hrs) \times 10^{-9}$$

Average NO_2 concentration was calculated from Q_{NO_2} and time of exposure.

The agreement with permeation tube values, and between individual samplers receiving identical exposures, was excellent. The calculation of results was greatly simplified because the NO_2 was apparently converted quantitatively to nitrite in the final determination, which was essentially that of Levaggi et al. (2) and Blacker (1). It was found more accurate and convenient, however, to combine all of the reagents and to add a single volume of combined reagent directly to the sampler. It was then transferred to a cuvette and read at 540 nm.

A number of trials were conducted in which samplers were mailed to cooperating laboratories, exposed by them, and returned to NYU for analysis. Results reported to the cooperating laboratory in ppm NO_2 x hrs and the NYU value obtained by dividing by the time of exposure were compared with the measured concentrations at the cooperating laboratory. All of the comparisons gave very good agreement, even one in which the samplers were mailed to Johannesburg, South Africa, and returned to New York for analysis. The concentrations used in these comparisons varied from fractional parts of a million up to several parts-per-million.

USE OF SAMPLERS FOR INDOOR AMBIENT MONITORING

In the course of the earlier work, it had been demonstrated that the samplers were quite stable both before and after sampling. This made possible the mailing of samplers to distant points while still obtaining satisfactory results. The standards for occupational exposure are, however, approximately 100 times higher than those for ambient air pollution by NO_2. It was concluded that the sampler would be satisfactory for measuring lower levels, however, if the time of exposure was increased from 1 working day to a full week. Using a 1-week exposure, a study (7) was carried out on 10 dwellings equipped with gas stoves and 9 with electric stoves. Since all of these dwellings were in the metropolitan New York area, all of the homes were centrally heated. It was found that the homes with gas stoves had very significantly higher NO_2 concentrations than did those with electric stoves. This was true both in the kitchen and nonkitchen areas. It should be pointed out that the level found in the kitchen of the gas stove dwelling was 49 ppb, which compares to the U.S. Primary Air Quality Standard of 50 ppb (annual average). Electric stove kitchens in this study, however, showed an average of about 8 ppb. A second study carried out in cooperation with a group in London (3) showed very similar results in two kitchens with gas stoves and two with electric stoves. A further study was carried out on homes in the Gainesville, Fla., area and included homes with 1) no unvented gas appliances, 2) gas stoves, 3) gas space heaters, or 4) combinations of gas stoves and gas space heaters. The results of this pilot study (to be published elsewhere) would indicate that the unvented gas space heater can be a significant contributor to indoor NO_2 concentrations.

Finally, outdoor air has been monitored on a weekly basis for 2 years on the 2nd and 14th floors of a building in Manhattan; these results are being analyzed.

CONCLUSIONS

It is concluded that the NO_2 sampler can be a very effective tool for the monitoring of this gas at ambient levels.

The device is light, inexpensive, maintenance-free, and can be satisfactorily exposed by untrained personnel.

A 1-week sampling period appears to be suitable for air pollution measurements.

The stability of the samplers, both before and after sampling, makes feasible their distribution by mail and return to a central laboratory for analysis. They therefore appear to be very practical for simultaneous measurement in a number of areas of either indoor or outdoor NO_2 concentrations.

ACKNOWLEDGEMENTS

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Discussion

MAGE: Before I take any questions, I would just like to make a comment. I think the diffusion coefficient is proportional to the square root of absolute temperature. So, you would expect the 1 percent increase with a 10° Fahrenheit rise. That would be about 2 percent change in temperature on the absolute scale. So, that would be a 1 percent increase.

PALMES: Per 10 degrees?

MAGE: You said Fahrenheit, and you got 1 percent.

PALMES: Well, the thing is that as the temperature rises, the volume also increases. That is one power. So, it actually goes $T^{-3/2}$ divided by T^{-1}, and so it goes by $T^{-1/2}$. It is thus absolute temperature to the one half.

ZISKIND: Richard Ziskind, Science Applications. I had never seen it addressed in health studies. Maybe you can tell me if any account was taken of the NO_2 level in the interior of the homes when they classified this as a high exposure/low exposure district. I wonder if that might be a real confounding factor that wasn't taken into account?

MAGE: I believe the classifications were according to the ambient levels of NO_2. If there is anybody here who would like to correct me, please do so.

WHITE: Otto White, Brookhaven Laboratories. It appears from the equations that if you increase the area or decrease the length that you increase the sensitivity. Is it that simple?

PALMES: It is that simple up to a point. If one gets down to a very short tube, then it starts behaving as if it were not quite so short. We have taken these down as low as 1 centimeter by using much smaller diameter tubes than this. But we have actually changed just the length in a tube of the constant diameter, and this has a direct linear effect.

If, however, you change both the diameter and the length, then we found that so long as we stayed above about 1 centimeter in length, then transfer could be predicted quantitatively.

GOLD: Avram Gold, Harvard School of Public Health. Have you ever considered the possibility of losses of the NO_2 onto the acrylic?

PALMES: We have certainly considered that, and we have tried the effect of storage on exposed samples and then analyzing them. We have done this for at least a couple of months after exposure and have obtained the same results.

In other words, once sampled, we can then measure for a very considerable period after exposure and still get the same results.

GOLD: I think that that was what I was wondering--essentially whether you have lost NO_2 into the wall during the sample that you would never get back?

PALMES: You are talking about the acrylic, not the plastic. Well, we get the theoretical transfer. Now, there might be a monolayer of NO_2 laid down onto the acrylic. I don't know.

Incidentally, we get exactly the same results with glass as we do with acrylic.

GOLD: Glass can soak it up. I have had some experience with this.

PALMES: I want to finish my story on this one. The first time we took these into a mine, they said we couldn't take them below ground. They wouldn't allow any glass down there. So, we stuck them on the wall. But after I got down there and saw these big loaders running around when we had only silly little lights on our heads--because otherwise they would never know we were there, and there is no place to hide--I thought, boy, glass or plastic is the last thing I would worry about.

DEBBRECHT: Fred Debbrecht, AID. Relative to the length versus diameter again, do you have a gut feel for the ratio that they must be to still preserve the diffusion effects?

PALMES: The A to L ratio is going to determine the sampling rate with the given coefficient of diffusion. Our sampler would have the equivalent sampling rate of approximately 50 ml per hour. The 3M sampler, which is again based on an air gap, has a sampling rate, as I recall, of around 30 ml per minute.

But in any event, it is almost a factor of 60 or so difference in this area to length ratio, so that it looks like it can vary quite widely. Now, if one is going to get involved with that, I think that the effect of turbulence is going to become much, much greater--that is my gut feeling on it.

SPENGLER: John Spengler. I am really fascinated by your measurements. Some of the measurements inside gas-cooking homes are very similar to the ones we have been making in our health study. But I encourage you to make outdoor measures simultaneously, because really the relative difference seems to be important. And have you noted whether you have seen an effect with venting in the kitchen? Because this apparently will change the value drastically in the gas-cooking homes that we have been measuring, as to whether there was venting or not in these kitchens.

PALMES: We did not check whether or not the gas stoves were vented in those which we measured. What we find generally is that people use the vent only when they are frying Chinese food or something that smells or gets a lot of splashing. In other words, it is not used to control the combustion gas part of it. We have not done this, but it certainly would make a difference; there is no question about that. Now, we have used this for outdoor measurements, but have been having difficulty finding good values with which to compare ours. We have 2 years of measurements in New York.

TURNER: Bill Turner. Do you know if your method is at all susceptible to NO interference?

PALMES: It is absolutely not susceptible to NO interference. We have modified this, and the article is in press now. So, we can use it for NO_x by converting the NO to NO_2 with the dichromate. But if you let it go through the screen, bounce off the dichromate, and then try to bounce back, it gets caught.

So, we can determine, then, both NO and NO_2 simultaneously. Of course, there are different coefficients of diffusion. But if you run one of these samplers along with an analytical sample, then you can determine their distribution.

In-Vehicle Air Pollution Measurements: A User's Perspective

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INTRODUCTION

Science Applications, Inc. (SAI) conducted measurements of gaseous pollutants in heavy-duty diesel tractors; transit, school, and mini-buses; taxicabs; and police cars. In performing these research programs and in planning future ones, we have concluded that in order to accomplish study objectives, a good deal of thought must be given to the selection of instrumentation and that compromise is expected. This manuscript will review our user experience in formulating and conducting in-vehicle air pollution measurements as they relate to the development and usage of personal exposure monitors.

The basic elements of two in-vehicle monitoring projects are summarized below. General conclusions are made about the objectives and requirements of such programs.

PROGRAM OVERVIEW--TOXIC GASES IN HEAVY-DUTY DIESEL TRUCK CABS

An experimental program was conducted for the U.S. Department of Transportation (DOT) to measure cab concentrations of toxic gases. Driver complaints, accident autopsy results, and very limited testing results motivated the DOT to sponsor this scoping study. Program components were to:

- Survey the heavy-duty diesel truck population and measure cab concentrations of toxic gases under a variety of conditions;

- Interpret the results in terms of short- and long-range driver health and performance effects.

PROGRAM OVERVIEW--CARBON MONOXIDE INTRUSION INTO THE PASSENGER AREA OF SUSTAINED-USE MOTOR VEHICLES

This study, sponsored by the Environmental Protection Agency, was specifically to look at the problem of carbon monoxide (CO) exposure in sustained-use vehicles such as school buses, taxicabs, police cars, etc. Here, the motivation for the study was similar in that incidents of drivers or passengers being overcome by CO had been reported, and concentrations in the 100-ppm range measured. The components of the study were to:

- Conduct a literature survey dealing with issues related to the problem--i.e., concentrations measured, causal factors of source and pathways, measurement approaches (biological and air concentration), and the concentration/effects relationship;
- Delineate factors affecting CO exposure, including vehicle design, operation control conditions, utilization characteristics, maintenance, and ambient control techniques;
- Conduct a limited sampling of vehicles in order to develop test protocol for a full-scale sampling program, observe the effects of postulated controlling factors, identify a worst-case subpopulation, evaluate instrument performance, and establish the range of CO concentrations within and among vehicles.

OBJECTIVES AND REQUIREMENTS--IN-VEHICLE POLLUTION STUDIES

Such studies can easily be seen to have a number of objectives. Phrasing these as questions, we may ask the following:

1) To which substances may a driver or a passenger be exposed?

2) How are these measured satisfactorily, including both biologically by performance or by instrumentation?

3) What are the sources of this exposure? How does it get to the driver or passenger?

4) What conditions control or affect exposure? Is vehicle self-contamination important?

5) Is any segment of the population at risk? If so, who and to what degree?

6) Are additional regulations needed? What form should they take?

Other questions could be posed; however, all of the above directly impact on instrumentation requirements. Specifically, in order to determine which substances may be present in the vehicle interior (Question 1), we could draw up the body of emissions measurements made up principally of exhaust analyses and urban ambient monitoring. This does not directly consider fuel evaporation and blowby. Nor does the emissions literature deal with differences in the source to interior transfer function among pollutant species. Secondary pollutant formation and photochemical or other conversion reaction rates are not well established between pollutant production and occupant exposure for the same vehicle. It would appear to be necessary to initially conduct a screening of the principal identified toxic emissions. This requires a variety of portable instrumentation which is preferably direct reading. Additionally, we must have a good deal of confidence that the error caused by interference of other substances in a detector is minimal or well known.

This brings us to Question 2. If substances act synergistically, is it more appropriate to measure performance indicators or physiological functions such as respiratory parameters? Even for a single pollutant such as CO, it is more direct to measure exposure effect or risk by blood carboxyhemoglobin (COHb) level through expired air or blood analysis sampling. However, in order to identify exposure levels for individual substances, and to determine pathways and dependence upon postulated factors, specific air sampling instrumentation is needed. In our initial effort to survey instrumentation for the continuous monitoring of CO, NO, NO_2, and hydrocarbons, 161 instruments were evaluated for 22 different performance characteristics. These 22 characteristics could be grouped into six general categories: simplicity, portability, dependability, reproducibility, ease of calibration, and stability.

Specifically, for our diesel tractor exposure study, we evaluated the particular needs of this program, such as the ability to quickly and easily perform a large number of idling and on-the-road measurements and the particular requirements of the diesel cab testing environment. We established the following requirements that the measurement system had to meet:

1) The instrumentation system had to be integrated into a single, relatively compact, and lightweight package with self-contained power supplies sufficient for continuous operation for at least 10 hours.

2) A system had to be capable of measuring ambient and truck cab level concentrations of carbon monoxide (CO), nitric oxide (NO), and nitrogen dioxide (NO_2), with required accuracy ($\pm$ 2 percent).

3) The system had to be capable of accurately and automatically recording the CO, NO, and NO_2 concentrations measured on a permanent record, so that the operating technician would have sufficient time to note and record the other important test variables and parameters (such as cab entry configurations, traffic and road conditions, and temperature and elevation), to readily sample ambient air, and to generally control the time-wise flow of the test program.

4) The instrumentation system and concentration levels recorded had to be insensitive to the vibration levels encountered in the diesel truck cabs, and they had to be relatively position- and orientation-independent (i.e., not require a flat horizontal surface for accurate instrumentation readings).

5) The system had to be capable of measuring any particular conditions (e.g., temperature and atmospheric pressure) that would affect the concentration readings. Power supplies for all components for the instrumentation system had to be quickly and easily rechargeable overnight by simple plug-in to any available 120-VAC source (e.g., a motel room outlet).

6) The system had to include internal pumps for continuously drawing the sample air through the measuring instruments, and to have a convenient set of lines and manifolding to enable easy sampling of the air at any location within the truck cabs (including sleeper cabs) and of the external ambient air environment. All such sampling lines and manifolding had to be constructed of materials that would not significantly alter the concentrations of CO, NO, or NO_2 in the air passing through them. The system had to include appropriate chemical scrubbers in the input to each instrument to remove potentially interfering constituents.

7) The system had to include small portable subsidiary devices for the measurement of external factors such as wind speed and direction, particularly for idling testing.

8) All electrical cables and devices carrying the concentration data signals from the three measurement instruments to the final recording point had to be shielded from spurious electrical signals (truck-generated and external), and the instrumentation system had to be fully capable of operation on either the self-contained power or external 120 VAC.

9) The instrumentation had to be able to respond quickly enough to track transients in the cab due to temporary conditions such as cigarette smoke, tunnel passage, road grades, etc.

10) The cab environment should not be contaminated by the instrumentation exhaust.

The specialized measurement system designed and constructed to meet the above requirement is shown in Figure 1 and is schematically illustrated in block diagram form in Figure 2. Air to be sampled is pulled in (from a cab

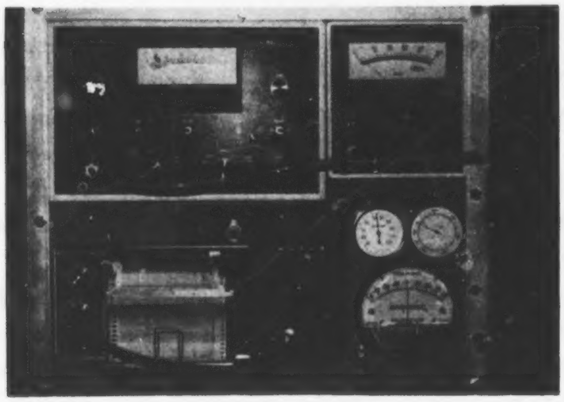

FIGURE 1. Continuous sampling instrumentation assembly.

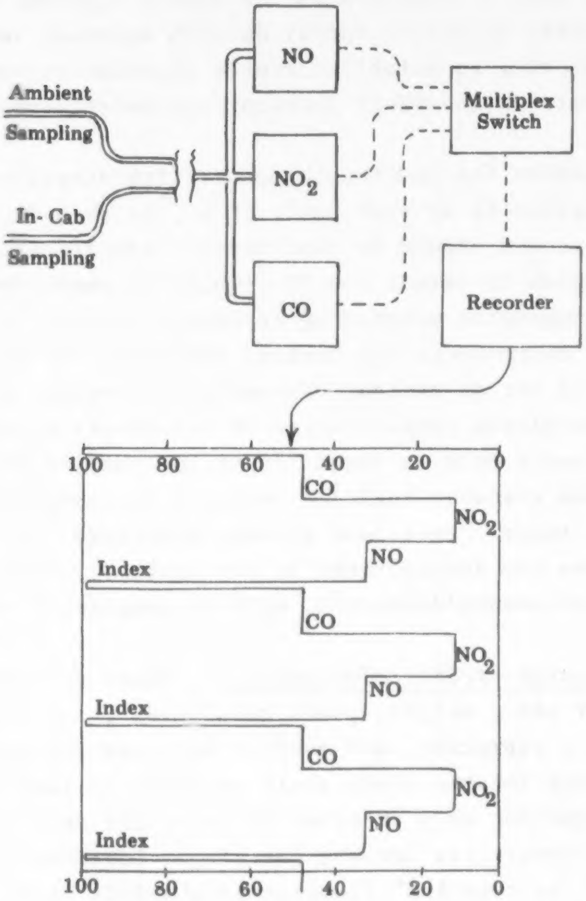
NO
Ambient
Sampling
Multiplex
Switch
NO_2
In- Cab
Sampling
CO
Recorder
100
80
60
40
20
0
CO
NO_2
NO
Index
CO
NO_2
NO
Index
CO
NO_2
NO
Index
100
80
60
40
20
0

FIGURE 2. Field measurement system and data output schematic.

interior location or the ambient external environment) through sampling lines and manifolding of Teflon and 316 stainless steel construction. The instruments are each direct reading, portable AC, or battery-operated gas analyzers with self-contained pumps, batteries, and battery chargers. The sensors are of the electrochemical voltametric type with linear output and direct reading in parts-per-million by volume. The instrumentation was verified to be position/orientation-independent and insensitive to electrical signal output vibration. The output signals were transmitted through shielded coaxial cable to a special multiplexing switch in order to allow the three levels to be recorded on one single-channel, lightweight, portable stripchart recorder. The instruments could be automatically sequentially cycled over an adjustable period or manually controlled.

We believe this type of approach is a suitable compromise when the study focus is divided between gathering survey data on exposure levels in a number of vehicles and attempting to establish source importance, mechanisms of intrusion, and parameters which affect interior concentrations.

In order to consider the previously posed fifth question--whether any segment of the population is at risk, and, if so, to what degree--a distinctly different testing approach should be considered. Specifically, as we formulated a sampling program to assess the CO problem in sustained-use vehicles, we developed a multisegmented monitoring approach. Initially, we surveyed the large variety of instruments and devices available for the measurement and detection of CO in air at ambient occupational levels. For the purpose of this study, we restricted consideration of relatively nonportable laboratory instruments to serve only as standards or for comparison purposes. Measurement approaches reviewed included portable CO instruments/detectors, biological monitors, tracer gases, and exhaust analyzers. Although all these measurement approaches are incorporated in the protocol, only the first category, portable CO instruments/detectors, will be considered here.

Portable CO Measurement/Detection Devices. These devices are identified by characteristics of size, weight, power requirement, and insensitivity to position, movement, vibration, and vehicle acceleration/deceleration. Suitable specifications for the class could be taken as less than 1 ft^3 volume, 15 lb weight, and requiring only external DC power (if any) or internal batteries with minimum 8-hour life between charging. Instrument bulk temperature range should span 40° to over 100° F, relative humidity up to 95 percent, and in-vehicle pressure range from up to 7,000-ft elevation, equivalent to slight overpressure due to ventilation blower. Accurate correction factor/charts should be available. Temperature correction/stability should separate sampled air temperature (0° to 100° F) in addition to the bulk instrument range. Suitable devices should ideally be free from significant interferences due to other gas species and from intermittent interferences caused by specialized conditions such as the electromagnetic wave environment due to CB radios, etc., operating in the near vicinity.

Classification of Portable CO Devices for Ambient-Occupational Use. Although maximum values of characteristics such as sensitivity, accuracy, etc., are nearly always desirable and sought after, the practical and sufficient level--from both test purposes and cost viewpoints--depends greatly on measurement purpose and objectives, the ultimate use of the data and overall results, and, of course, the present state of technology. For example, the least sensitivity and accuracy would be required of simple indication/detection devices used in large population sampling, or of limited detection uses where the device would be affixed to the vehicle interior to indicate the presence of CO concentrations exceeding some limit value, such as 35 ppm. Such a device would require minimal sensitivity of approximately the limit value--for example, 35 ppm--and an accuracy of perhaps ± 25 percent.

In order to span the broad use/purpose and performance characteristic spectrum of portable CO measurement/detection devices of potential in-vehicle use, the devices have been categorized in four use/effectiveness classes. The classes are: continuous analyzer, cumulative dosimeter, intermittent/spot sampler, and limit detector. The basic use, measurement techniques, and the approximate overall ranges in physical characteristics, performance specifications, and costs for each of the four classes are listed in Table 1.

The continuous analyzer class includes relatively high-performance portable instruments capable of continuous CO concentration measurements and of providing output for continuous recording. Some are position/orientation sensitive due to the particular design of the liquid electrolyte or use of humidifying reservoirs in the internal sampling stream. This type will be used in a selected subgroup of the sustained-use vehicles to conduct a detailed investigation of particular vehicles to determine effects of various factors (exhaust system condition, ventilation effects, leak paths, ambient levels, the spatial concentration distribution in the vehicle, etc.). These instruments should approach performance characteristics of stationary monitoring/laboratory instruments, such as 1 or 2 ppm sensitivity and ± 1 or 2 percent accuracy.

TABLE 1

Classification of Portable CO Measurement/Detection Devices
and Summary of Characteristics

CLASS	CONTINUOUS ANALYZER	CUMULATIVE DOSIMETER	INTERMITTENT/SPOT SAMPLER	LIMIT DETECTOR
Measurement Type	Continuous	Cumulative	Instantaneous	Limit Detection
Measurement Principle	Electrochemical Infrared Catalytic Combustion Gas Filter Correlation	Electrochemical Stain Tube/Pump Colorimetric Tube/Pump Stain Tube	Electrochemical Stain Tube/Hand Pump Colorimetric Tube/ Hand Pump	Colorimetric Indicator Badge Ceramic Disc
Accuracy	± 1 to ± 5 percent	± 15 to ± 25 percent	± 2 to ± 25 percent	± 25 percent at best
Sensitivity	0.1 to 2 ppm	1 to 100 ppm-hr	2 to 10 ppm	50 to 200 ppm
Range	0-50 to 0-1,000 ppm	1-100 to 10-3,000 ppm 1/2 hr to 7 days 0-999 ppm-hr	0-50 to 10-1,000 ppm	N/A
Size	0.1 to 1 ft^3	Shirt Pocket	Pocket to 0.2 ft^3	Pocket, Badge
Weight	3 to 20 lb	1 oz to 1 lb	1/2 to 2 lb	1/2 to 2 oz
Position Sensitivity	Some	No	Some	No
Power	Battery	Battery/None	Battery/Human	None
Cost Range	$600 to $4,000	$1 to $600	$100/$1,000	$1 to $5
Typical Cost	$600 Catalytic, $1,200 Electrochemical, Higher for Others	$500 Electrochemical, $250 Tube/Pump, $1 Tube (Plus reading device)	$250-$1,000 Electrochemical $90 Tube/Hand Pump	$1

Portable CO measurement devices of the cumulative dosimeter class are distinguished by providing a cumulative measure of CO exposure. These personal air quality monitors are designed to be attached to an individual, without interfering significantly in normal activities, sampling air in the breathing zone, and providing a cumulative CO dosage measurement over the sampling time. Several different measurement principles have been employed, including:

- Electrochemical cell types with solid state electronics,
- Stain tubes with air throughput by pocket-size sampling pumps, and
- Nonaspirated stain tubes.

Sample times can range from one-half hour to days among the categories. Position insensitivity is critical, as is the operating time between battery recharges or replacements. This equipment class will provide an important part of the program for several reasons. They measure actual CO exposure and dosage for the individual during normal activities. They do not require continuous technician presence. They can provide nearly simultaneous data to allow comparison across several groups.

Additionally, we will utilize nonaspirated stain tubes to measure integrated exposure in a large number of vehicles. These inexpensive devices will be used as a screening tool to survey randomly selected vehicles in various fleets and locations in order to investigate for hot spots and establish sampling strata for more expensive and intensive subsequent testing.

Devices of the intermittent/spot sampler class provide the capability of measuring the instantaneous CO concentration at the specified sample location. They differ from the continuous analyzer class, which also includes an instantaneous measurement capability, by the fact that they are typically more portable, less expensive, and do not provide a continuous recording capability.

The limit detector class includes devices which can be attached to an individual or a fixed location. They provide a positive indication of exposure to CO concentrations above some design levels. Some school buses are currently equipped with such devices, which are checked periodically to see if a particular CO level was exceeded.

In Summary. Devices in each of the four classes described above may have an application in a measurement program. The selection of an appropriate class of device or combination of classes will depend on the measurement purpose and objectives, the ultimate use of the data in overall results, and, of course, the study's size and funding.

Needs that we have identified in personal samplers, related to their utilization for in-vehicle pollution studies, include a sensitive range, nitrogen dioxide (NO_2) personal cumulative dosimeter, and a respirable fraction particulate personal sampler.

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Discussion

MEIER: Eugene Meier, EPA, Las Vegas. Why do you say that you need very sensitive NO_2 dosimeters, in this particular case from the health point of view?

ZISKIND: In our diesel truck study, of the gases that we measured, we found NO_2 levels to be the closest to the levels of known toxic effects.

MEIER: Was it exceeding these levels or just close to them?

ZISKIND: Well, it can exceed a criterion level momentarily. But in general, it was highly time dependent and condition dependent. That is, we could see that it would be very useful to have a personal sampler rather than an electrochemical detector or instrument so that we could do more of a survey to really identify more explicitly the conditions of NO_2 emission leading to these levels.

MAGE: David Mage, EPA. What standard was being violated? Was it an occupational standard or an ambient standard?

ZISKIND: It was an occupational standard. If I am contrasting it with the NIOSH proposed standard of one part-per-million and a half part-per-million action level ceiling, then that was commonly found to be violated where we considered the ambient and the vehicle contribution.

If we considered the public secondary or primary standards, that was violated all the time.

MEIER: So you are saying it was a relatively high concentration of NO_2?

ZISKIND: We are talking about trucking operations that in this case are located in urban areas. And specifically, we did the Southwest, and then we are driving along on crowded freeways. We are getting a lot of NO_2.

MEIER: Then relate that back again to buses.

ZISKIND: We haven't made any NO_2 measurement on buses--only on diesel trucks.

MEIER: So, it is primary occupational at this time in terms of truck drivers?

ZISKIND: In terms of truck drivers, yes.

We are taking ambient levels, and we are taking in-vehicle levels. We are trying to look at the difference. And we are also looking at the people who are driving along right next to these trucks. And they are both the cause of emissions, and, also, the people are getting some NO_2 from the trucks.

WILLIAMS: Marsha Williams, EPA. I am curious about the CO results on the diesel trucks because I would expect, just due to the emissions from the diesel trucks, that you would see much higher interior NO_2 levels in trucks than you would CO, relatively speaking, because of what they are putting out.

ZISKIND: That is right.

WILLIAMS: So, I am curious about what the CO results were. And the other thing is: What kind of data capture did you have on the instrumentation of your trucks? You lose a tremendous percentage of your data just due to instrument problems with vibration and such.

ZISKIND: Well, we had the equipment shock mounted. And we were monitoring continuously.

WILLIAMS: Do you know what kind of capture rate you had, then?

ZISKIND: We manifolded these things. So, we alternated one, two, and three in the instrumentation. We came back to each one. Not too much happens between readings. We get a pretty good square wave. It is constant for 20 seconds. Sometimes you get fluctuations when something drives by.

What we were looking for was driving along and setting up a different condition. The condition may be speed; it may be vents, heater, air conditioning, or something like that. We were looking at what the effect is.

So, we looked for the equilibrium to be reached, and then it is reached. And then we say go on to another condition. We got essentially 100 percent capture, if I can be so bold as to make that statement. But we didn't have any loss on that method.

You are right about the conclusion. Carbon monoxide in diesel trucks did not appear to be as significant as in gasoline vehicles.

Calibration of Personal Exposure Monitors for Personal Exposure and Health Effect Studies

Charles L. Kimbell
Houston Atlas, Inc.
Houston, Texas

BACKGROUND

Standard reference gas mixtures are required to calibrate personal exposure monitors. This paper describes a device whereby a low parts-per-million (ppm) mixture of carrier gas and pollutant can be generated in minutes with ± 1 percent accuracy.

In the past, compressed cylinder mixtures, permeation tubes (2), dynamic flowmeter blending, or exponential dilution techniques were used. These methods require long lead times of several weeks for preparation and careful adjustments, and they cannot easily be converted for use over wide ranges or to use with different gases. Permeation tubes require close temperature control and are subject to inaccuracies which have not been adequately described in the literature.

The data shown in Figure 1 illustrate errors associated with permeation devices. Long-term stress on Teflon causes creep, resulting in a change in permeation rate over a period of days. Temperature changes cause excessive permeation rate change, except in controlled laboratory environments and with good temperature controls.

STANDARD REFERENCE SAMPLE GENERATOR

This paper describes a Standard Reference Sample Generator (1) that is ideally suited to preparing ppm samples of any trace gas in any carrier gas.

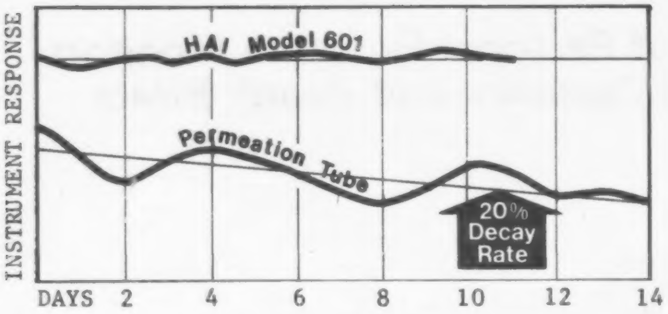


FIGURE 1. Plot of ppm generator by Model 601 and by permeation tube.

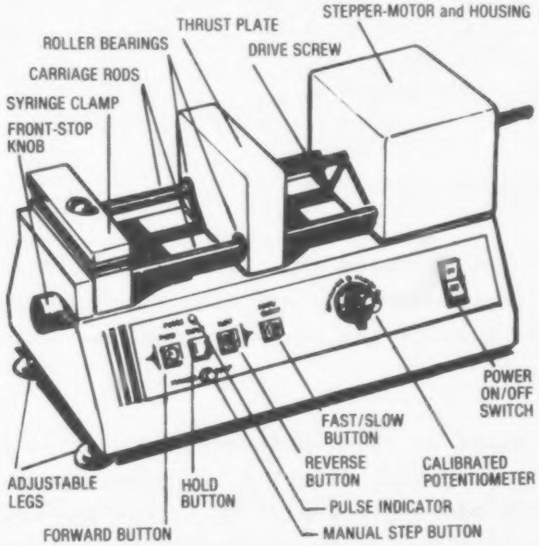

STEPPER-MOTOR and HOUSING
THRUST PLATE
DRIVE SCREW
ROLLER BEARINGS
CARRIAGE RODS
SYRINGE CLAMP
FRONT-STOP
KNOB
POWER
ON/OFF
SWITCH
FAST/SLOW
BUTTON
REVERSE
BUTTON
CALIBRATED
POTENTIOMETER
ADJUSTABLE
LEGS
HOLD
BUTTON
PULSE INDICATOR
FORWARD BUTTON
MANUAL STEP BUTTON

FIGURE 2. Precision syringe drive.

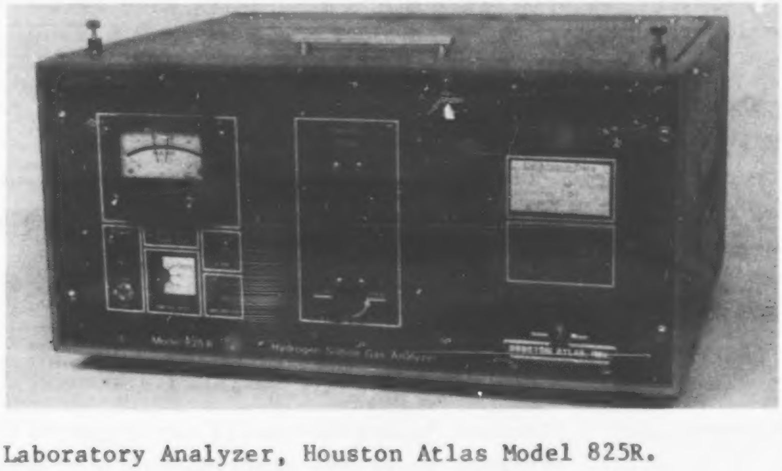

Model 825 R
Hydrogen Sulfide Gas Analyzer

FIGURE 3. Laboratory Analyzer, Houston Atlas Model 825R.

The equipment can be removed from storage, and, within minutes, a continuously flowing gas mixture is available either for short-term use or for continuous flow for an indefinite period. The only materials required are reagent-grade pure trace gas and a carrier gas of a volume slightly greater than the amount of sample required.

This convenient method of preparing any type of ppm mixture is well adapted to calibration of personal exposure monitors and instruments, and for generation and maintenance of known atmospheres in environmental chambers. When an enclosure is purged, with a flowing trace gas mixture of four times the enclosure volume, then the trace gas in the enclosure will be within 2 percent of the original ppm mixture. The trace gas generator can continue purging the enclosure and will eliminate any deterioration of the environmental chamber contents by absorption or adsorption.

PRINCIPLE OF OPERATION

The Standard Reference Sample Generator is basic in its operation. A volumetrically metered minute quantity of trace gas is mixed with a continuously flowing fixed quantity of carrier gas.

Minute quantities of gas are very difficult to accurately produce with the usual flow devices. The sample generator uses a microliter sampler to incrementally inject a fixed volume of trace gas into the flowing carrier. Accurate timing and rapid injection result in ppm mixtures that are accurate to ± 1 percent. Labyrinth mixing results in a uniformly blended sample. An alternate to the microliter sampler method of injecting trace gas is to use a precision-type syringe drive actuated by a synchronous stepping motor (Figure 2).

VERIFICATION OF SAMPLE

To determine accuracy and long-term stability of the Reference Standard Generator, a stable analyzer was required. A Model 825R Houston Atlas hydrogen sulfide (H_2S) analyzer was used. (See Figure 3.) The unique first-derivative principle of operation provides stable zero and span even at low ppm. (See Figure 4.) Linearity of response and accuracy (Figure 5) allowed accurate measurements. The data shown in Figure 1 above were obtained in this manner.

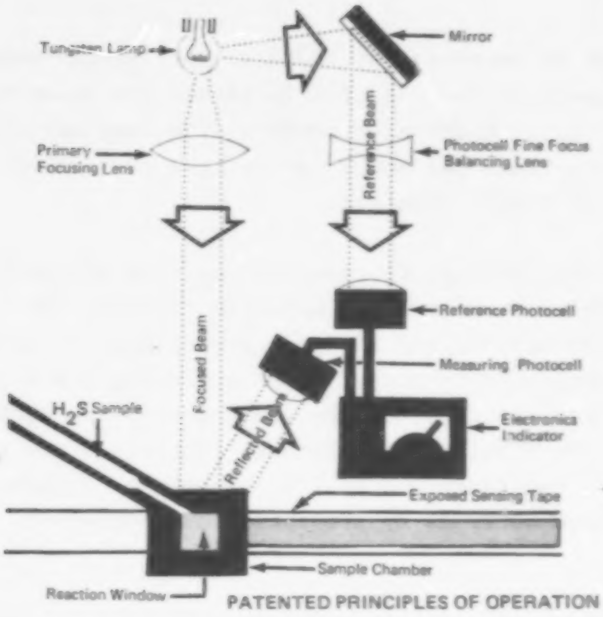

Tungsten Lamp
Mirror
Primary Focusing Lens
Reference Beam
Photocell Fine Focus Balancing Lens
Reference Photocell
Focused Beam
Measuring Photocell
H_2S Sample
Reflected Beam
Electronics Indicator
Exposed Sensing Tape
Sample Chamber
Reaction Window
PATENTED PRINCIPLES OF OPERATION

FIGURE 4. Rate reading analyzer principle.

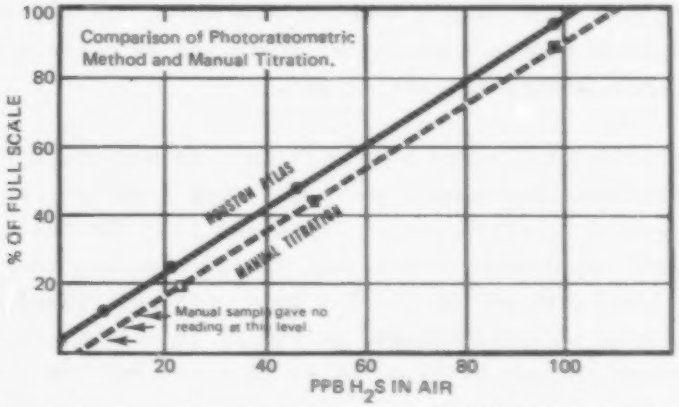
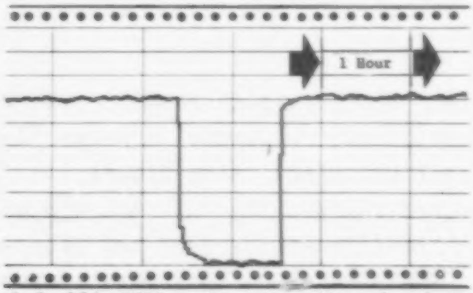


FIGURE 5. Comparison of Houston Atlas Model 825R H_2S Analyzer and manual titration analysis.



TEST: Model 601 PPM Reference Standard Generator

FIGURE 6. Sample generated by Houston Atlas, Inc., Model 601 Reference Standard Sample Generator.

RESULTS

Chart recordings verified the repeatability, accuracy, and long-term stability of this method for generating trace gas mixtures. Figure 6 is a chart recording of the sample generated by the Houston Atlas, Inc., Model 601 Reference Standard Sample Generator. The analyzer provided sample and hold readings every 3 minutes. This recording shows a 5-hour run with a 1-hour shutdown period. Note that no overshoot occurs and that a stable reading is obtained in minutes. This proves that long-term storage does not interfere with ready availability for quick use.

This system easily lends itself to automatic verification and calibration of continuous monitors. Several installations in the field have proven dependability during more than a year of unattended operation.

This parts-per-million generator can also easily provide parts-per-billion samples intermittently or continuously. The simplicity and ease of operation allows handling by laboratory technicians. No delicate accessory equipment, such as a microgram balance, is required. This enhances portability and field worthiness.

Personal monitors can be calibrated and their accuracy verified by feeding sample directly to the monitor or by placing it in a chamber whose environment is maintained constant by continuous flow from the ppm generator.

This equipment removes the calibration and verification of equipment from the realm of the research laboratory to that of a practical field tool for day-to-day use by technicians in the field.

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1. Kimbell, C.L., Method of Testing an Analyzer to Determine the Accuracy Thereof and a Volumetric Primary Standard Apparatus for Doing the Same. U.S. Patent No. 4,114,419.

2. O'Keeffe, A.E., Gas Dispensing Device. U.S. Patent No. 3,412,935.

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A New Family of Miniaturized Self-Contained CO Dosimeters and Direct Reading Detectors

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Harry G. Wheeler, and John Martin
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General Electric Company
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INTRODUCTION

The Direct Energy Conversion Programs component of General Electric (GE) Company has been engaged since 1958 in the development of solid polymer electrolyte technology for use in water and brine electrolysis, oxygen concentrators, fuel cells, and toxic gas sensors. In 1962-1966, fuel cells were produced for the Gemini spacecraft program. In 1964-1968, an improved version of the Gemini fuel cell was used on the Biosatellite spacecraft program. As GE fuel cell technology advanced, other applications of this technology were developed.

In 1972, using this technology, General Electric introduced a small commercial hydrogen generator for laboratory instrumentation and chromatographic applications. This small (<1 cu ft), high purity hydrogen generator produced laboratory hydrogen safely and on demand, eliminating the need for hazardous hydrogen cylinders in the laboratory.

The feasibility of a miniaturized hydrated solid polymer electrolyte sensor cell was demonstrated with hydrogen in 1965 (1). Polarographic and potentiostatic techniques of maintaining the sensing electrode at a fixed voltage versus a stable reference electrode were shown. This effort was extended to the detection of carbon monoxide and other toxic gases, as reported in 1971 (2). Prototype carbon monoxide (CO) instruments specifically designed for mine use were developed under a Bureau of Mines contract (3,4).

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In a CO sensing instrument, a measurable electrical current is generated through electrochemical reaction of the contaminant gas at the potential controlled electrode. The sensor can be designed to selectively detect NO, NO_2, H_2, H_2S, SO_2, ethanol, and other gases, depending upon the biasing voltage placed on the cell, the sensing electrode composition, and the scrubber system for removal of interfering gases.

The electrochemical cell is particularly adaptable to small, portable personal dosimeters (5) and detectors, as the cell can be miniaturized and can be used with solid state electronics, lightweight pumps, and rechargeable battery systems. The major significance of the specific electrochemical cell as a sensor is the reduction in size and weight of the instrument. Now possible are pocket personal dosimeters and small, lightweight belt or strap-carried detectors weighing 1 pound or less; the final unit size is limited by the additional features of readout, alarms, etc., rather than sensor size.

Figure 1 shows a photograph of the new family of miniaturized portable instruments developed by GE for the detection and monitoring of CO levels in air. From left to right are the support console, personal dosimeter, hand-held direct reading detector, and detector case with carrying straps.

CELL SYSTEM

The heart of any gas detection device is the sensor or transducer. These instruments utilize a hydrated solid polymer electrolyte membrane cell (Figure 2) in an electrically biased fuel cell mode. The cell generates an electrical signal proportional to the CO concentration of the sample gas in the cell, and displays excellent stability over long operating periods. Circuit compensation is provided to correct for shifts in sensor span signal due to temperature changes; no zero compensation is required.

The fuel cell utilized is packaged in a housing 1.51 in wide x 1.0 in deep x 0.92 in high. The solid polymer electrolyte membrane, which is approximately 0.01 in thick, serves as both an electrolyte and separator. Bonded to the membrane on one side are the gas sensing and reference electrodes (the sensing electrode is directly exposed to the sample), and the current collecting counter electrode on the other side. The second side is also exposed to a renewable supply of distilled water from the reservoir, since the membrane functions only when hydrated. Lexan® plastic support members hold the membrane cell in position, while directing the gas flow over

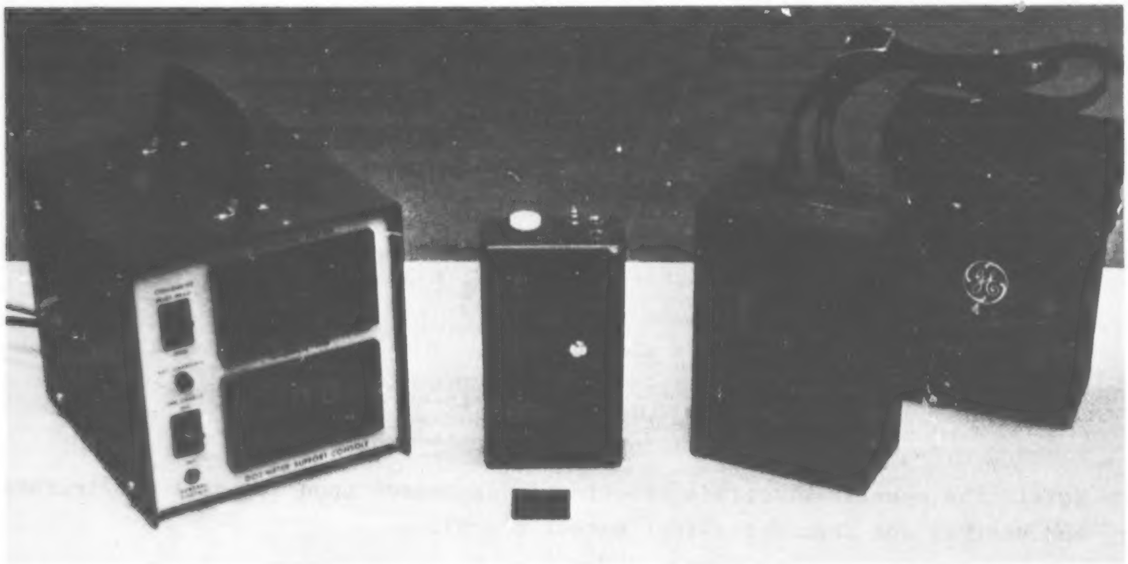
DOSIMETER SUPPORT CONSOLE

FIGURE 1. Carbon monoxide instrument family.

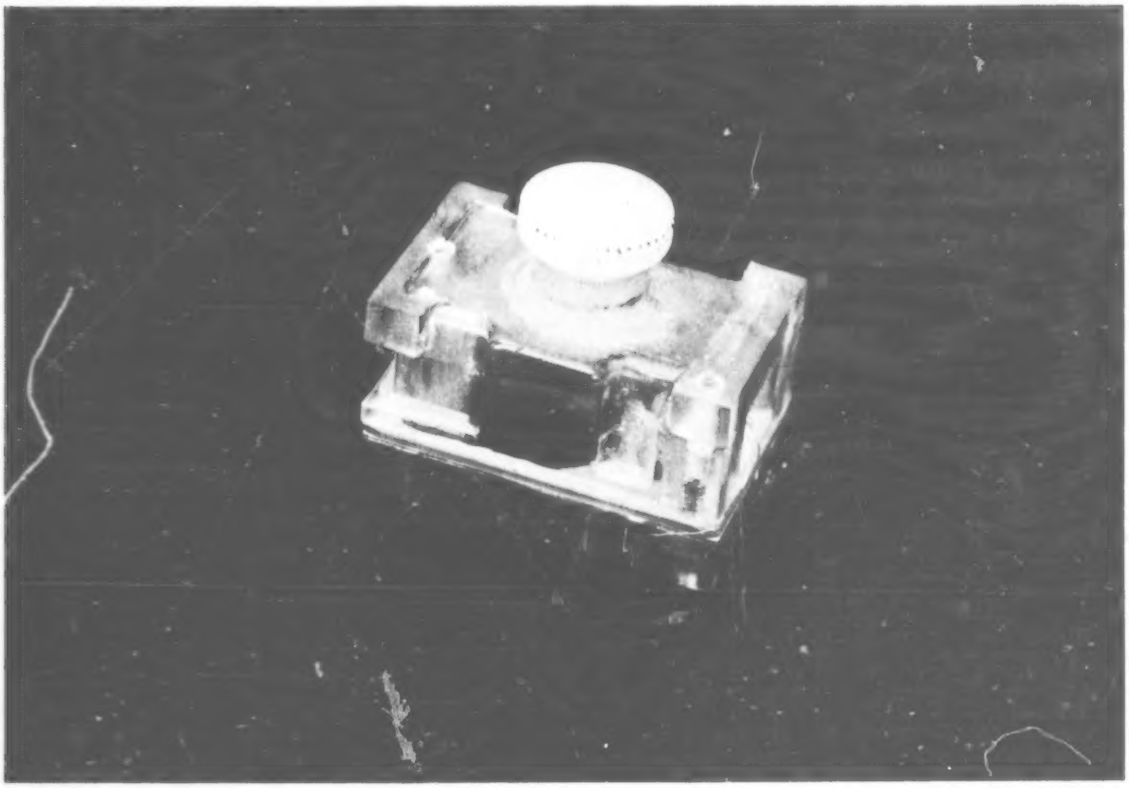

FIGURE 2. Detector and dosimeter cell.

the sensing electrode and the water flow to the counter electrode. The sensing electrode of the cell is held at a fixed predetermined anodic voltage using an efficient electronic control circuit.

As with conventional fuel cells, the relevant reactions are:

1) Sensor electrode

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e$$

2) Counter and reference electrodes

$$2e + 1/2\ O_2 + 2H^+ \rightarrow H_2O$$

Note: the counter electrode reaction is dependent upon the cell configuration and design, and does not affect output signal.

The hydrated solid polymer is extremely efficient, durable, stable in long-term response to CO, and has a low background (zero CO) current. Unlike cells employing liquid acid or alkaline electrolyte, there is no need for electrolyte normality control; the hydrated cell unit is stable to extreme variations in humidity. No corrosive electrolytes are added to the cell; the only routine maintenance needed for cell operation is the periodic filling of the water reservoir with distilled water.

SYSTEM INSTRUMENTATION

A system schematic for the direct reading detector and personal dosimeter is shown in Figure 3. In both units, the CO containing gas sample flows through the dust filter and gas scrubber chamber, then through the pump, sensor cell, and rotameter (flow indicator), and is subsequently vented. The pump speed is set to 60 cc/min by a trim adjustment. Although the sensor response is somewhat sensitive to sample flow rate (see the Operational Test Results section), field experience has shown the flow system to be remarkably stable, and trimming is required very infrequently.

The filter and gas scrubber serves to remove small particles of dust from the flow system as well as removing interferant gases which might affect the output of the cell assembly. Potassium permanganate on alumina is used for gas scrubbing; the effectiveness of this scrubber for potential interferant gases is shown in Table 1. The scrubber material should be changed

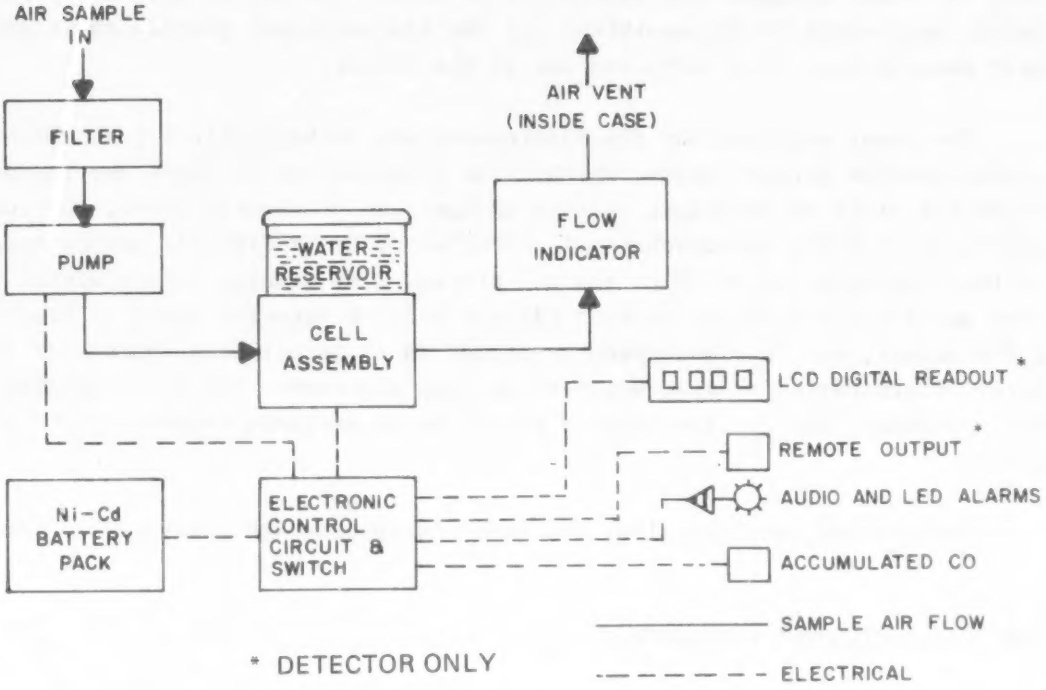
AIR SAMPLE IN
FILTER
PUMP
WATER RESERVOIR
CELL ASSEMBLY
FLOW INDICATOR
AIR VENT (INSIDE CASE)
LCD DIGITAL READOUT *
REMOTE OUTPUT *
AUDIO AND LED ALARMS
ACCUMULATED CO
Ni-Cd BATTERY PACK
ELECTRONIC CONTROL CIRCUIT & SWITCH
SAMPLE AIR FLOW
ELECTRICAL
* DETECTOR ONLY

FIGURE 3. System schematic.

TABLE 1

Effect on Instrument CO Response by Potential Interferants

INTERFERANT* GAS	GAS CONC. IN AIR	EQUIVALENT CONC. (PPM) OF CO
H_2O VAPOR	50 to 100% RH	0
O_2	16 to 90%	0
CH_4	3%	0
CO_2	1%	0
NO	50 PPM	0
NO_2	10 PPM	0
SO_2	25 PPM	0
H_2	100 PPM	2
C_2H_2	100 PPM	16
HCHO	5 PPM	0
H_2S	10 PPM	0
C_2H_4	100 PPM	18

*$KMnO_4$ ON ALUMINA (PURAFIL) FILTER

when the color changes from red-purple to brown. As can be seen from the table, only ethylene and acetylene (of the listed gases) provide any significant interference to CO with the use of the filter.

The power supplies for the instruments are rechargeable 5.2 V, 250 MA-hr nickel-cadmium battery packs, which allow a minimum of 10 hours continuous operation after an overnight battery charge. As previously noted, the current resulting from the electrochemical oxidation of CO is directly proportional to the concentration of CO in the gas stream. The ensuing output signal is then amplified for visual readout (direct reading detector only) or visual/audio alarms, and is simultaneously stored in an integrating coulometer for later determination of time-weighted average exposure. The detector also has an output jack for providing a signal to an external recorder (0 to 1 volt).

Operational specifications for both instruments are presented in Table 2.

SPECIFIC INSTRUMENT PARTICULARS

Both the direct reading, hand-held detector and the personal dosimeter utilize many common primary components (i.e., pump, sensor cell, flow indicator) and have similar features (i.e., 5.2 V nickel-cadmium battery pack, filter system, alarm system, accumulated CO readout); however, each unit was specifically designed to handle different tasks. A tabulation of instrument particulars is presented in Table 3. Details of the design characteristics of both instruments follow.

Direct Reading Detector

The miniaturized portable self-contained direct reading detector was developed for use in a wide variety of applications, including: 1) to be worn by individuals for immediate personal assessment of carbon monoxide in working areas such as mines, factories, motor vehicles, etc.; 2) to be used as a portable continuous area monitor; 3) to be used as a personal dosimeter for obtaining time-weighted average exposure to CO; 4) to be used in conjunction with a recorder for obtaining a permanent, continuous record of CO exposure. The detector (Figure 4) has many features, including a one-half-inch LCD digital readout (0 to 1,000 ppm CO) which is readily visible at the top of the case. The instrument is lightweight (1.1 lb), small (5.9 in high x 3.8 in wide x 2.3 in deep), and is totally self-contained with

TABLE 2

Carbon Monoxide Instrument Specifications

CARBON MONOXIDE INSTRUMENT SPECIFICATIONS

ACCURACY	± 10% FOR RANGE 0-500 PPM CO UNDER THE FOLLOWING CONDITIONS: TEMPERATURE: 1-40°C ORIENTATION WITHIN 45° OF VERTICAL RELATIVE HUMIDITY: 0-100% DAILY ZERO AND SPAN CALIBRATION OXYGEN LEVELS ABOVE 16% INTERFERENCE COMMONLY FOUND IN AMBIENT AIR, NO, NO_2, H_2S, SO_2, NH_3, CO_2, DUST, ETC.
INSTRUMENT RANGE	0-1000 PPM
WARM-UP TIME	15 SECONDS (2 MINUTES – DOSIMETER)
INITIAL ACTIVATION TIME	14 HOURS TO FULL ACCURACY
RESPONSE TIME (90%)	< 2 MINUTES
SPAN DRIFT	± 10% (1 WEEK)
ZERO DRIFT	± 2 PPM (10 HOURS)
STORAGE TEMPERATURE RANGE	1 TO 50°C
OPERATING TIME WITHOUT RECHARGE	10 HOURS (4 HOURS WITH ALARMS ON)
TRANSDUCER LIFE	MINIMUM OF 6 MONTHS
CONSUMABLES LIFE	MINIMUM OF 1 WEEK
SAFETY	DESIGNED TO MEET THE MECHANICAL AND ELECTRICAL SAFETY REQUIREMENTS OF APPROVAL AND TESTING, MSHA SCHEDULE 2G

TABLE 3

Instrument Particulars

	15ECS3CO Hand Held Detector	15ECS1CO Dosimeter
1. DIMENSIONS		
LENGTH	5.9 in.	5.3 in.
WIDTH	3.8 in.	2.9 in.
DEPTH	2.3 in.	1.4 in.
2. WEIGHT	1.1 lbs.	0.63 lbs.
3. BATTERY PACKS	5.2 VDC, 250 MA-HR., RECHARGEABLE NI-CD	
4. USEFUL RANGE	0-1000 PPM CO	0-1000 PPM CO
5. LOWER DETECTABLE LIMIT	1 PPM CO	1 PPM CO
6. DIRECT READING LCD IN PPM	YES	NO
7. ACCURACY		
DIRECT READING	<± 10% OVER 0-500 PPM RANGE	
INTEGRATING COULOMETER	±10% OF 8 HRS. TIME WEIGHTED AVERAGE	
8. ALARMS	RED LIGHT WARNING AND AUDIBLE ALARM @ 200 PPM CO	AMBER LIGHT WARNING @ 100 PPM CO RED LIGHT WARNING AND AUDIBLE ALARM @ 200 PPM CO
9. SELF-CONTAINED	YES (NO ADDITIONAL PUMPS, FILTERS, BATTERIES, ETC. FOR OPERATION)	YES
10. ADDITIONAL FEATURES	SELF-TEST REMOTE READOUT OPTION EARPLUG ATTACHMENT LOW BATTERY SIGNAL	SELF-TEST

its own pump, filter system, and rechargeable battery pack. A leather carrying case with shoulder strap or belt mount is available.

The carbon monoxide detector controls, adjustment points, and performance observation windows are shown in Figure 5. The unit contains both visible and audible alarms set normally for 200 ppm CO, and an earphone connection

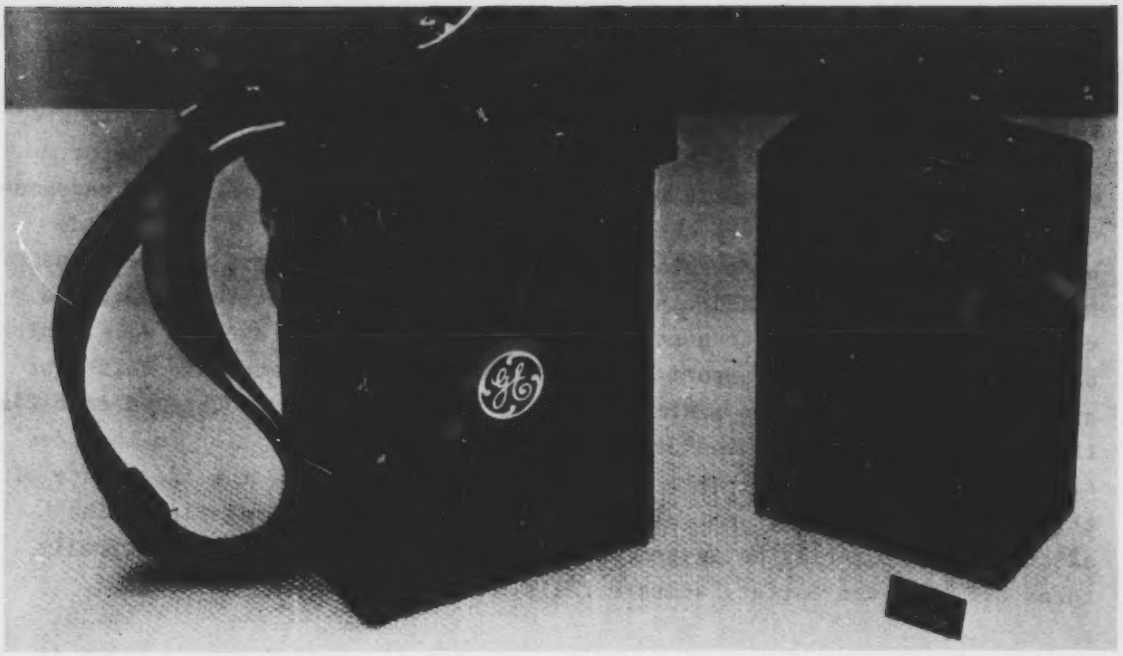

FIGURE 4. Detector and case.

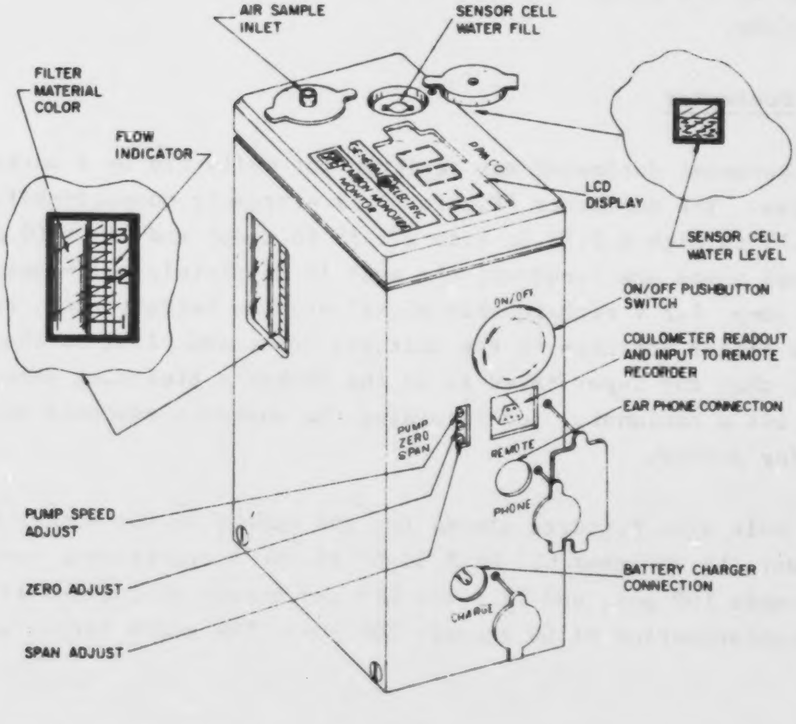
AIR SAMPLE INLET
SENSOR CELL WATER FILL
FILTER MATERIAL COLOR
FLOW INDICATOR
PPM CO
GENERAL ELECTRIC
CARBON MONOXIDE MONITOR
LCD DISPLAY
SENSOR CELL WATER LEVEL
ON/OFF
ON/OFF PUSHBUTTON SWITCH
COULOMETER READOUT AND INPUT TO REMOTE RECORDER
EAR PHONE CONNECTION
PUMP
ZERO
SPAN
REMOTE
PHONE
PUMP SPEED ADJUST
ZERO ADJUST
BATTERY CHARGER CONNECTION
CHARGE
SPAN ADJUST

FIGURE 5. CO detector controls and adjustment points.

for operation in noisy areas. Windows are available in the case for observation of pump speed on a rotameter, the color of the filter material, and the distilled water level in the sensor cell. Distilled water fill and air inlet sample ports are visible on the top of the case. Conveniently located on the side of the case are the off-on pushbutton switch, the coulometer readout and input to a remote recorder or readout (0 to 1 volt), the earphone connection, and the battery charger connection. Also located on the side of the case for convenient setting are the pump speed adjust, and zero and span adjust screws. In addition to a direct LCD readout of CO in ppm, the unit contains an integrating coulometer for time-weighted average data, which can be read out on the Support Console. The unit also features a self-test circuit which enables the alarms and amplifying system to be checked each time the unit is turned on. In addition, approximately 1 hour prior to the need for battery recharge, a low battery warning is provided by the appearance of three decimal points, a semicolon, and an arrow on the LCD display. The alarms are momentarily activated, and the instrument display automatically turns off when the battery voltage falls below a predetermined level.

Calibration of the direct reading detector is carried out as shown in Figure 6. A zero and span gas cylinder kit is optionally available from General Electric Company. The regulator on the calibration kit is set for 150 cc/min. The pump on the unit will draw 60 cc/min of zero or span gas. Adjustment of the direct readout is made by setting the zero and span pot adjust screws.

Personal Dosimeter

The personal dosimeter was designed for daily use by a worker in a hazardous area. The dosimeter (Figure 7) is extremely compact--being pocket-sized (4.75 in high x 2.75 in wide x 1.38 in deep) and light (0.6 lb). No external pumps are required; the unit is completely self-contained with built-in pump, 5.2 V rechargeable nickel-cadmium battery pack, and alarms. The small filter attaches to the unit air input and clips to the worker's collar so that the input taken is in the worker's breathing zone. The instrument has a coulometer for recording the worker's exposure to CO during the working period.

The unit also features alarms for the safety of the worker which respond as follows: 1) an amber LED will light if the instantaneous concentration of CO exceeds 100 ppm, and 2) a red LED and buzzer will alarm if the instantaneous concentration of CO exceeds 200 ppm. The alarm levels are preset

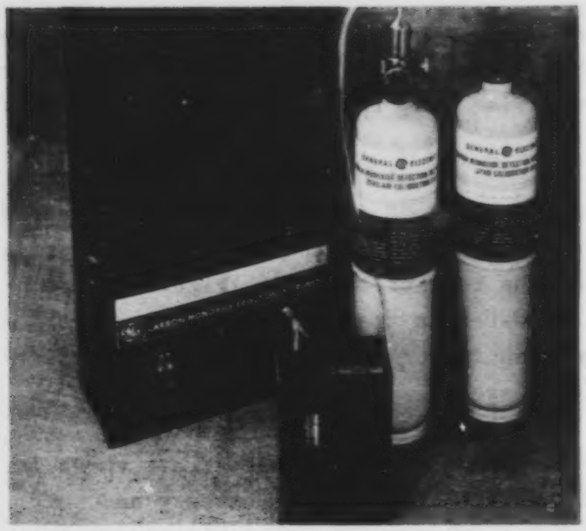

FIGURE 6. Calibration of direct reading detector.

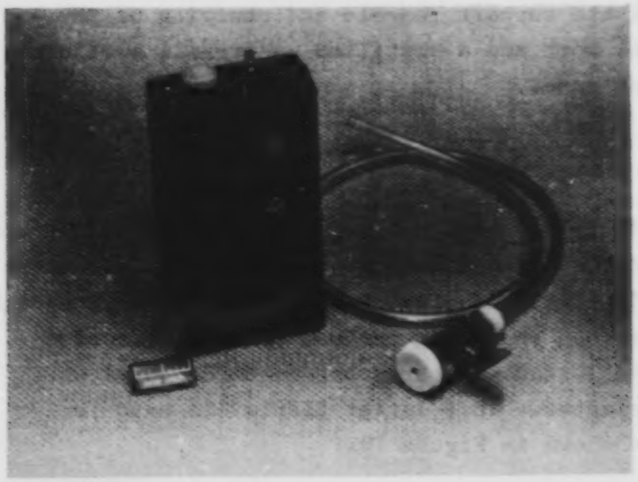

FIGURE 7. Carbon monoxide dosimeter.

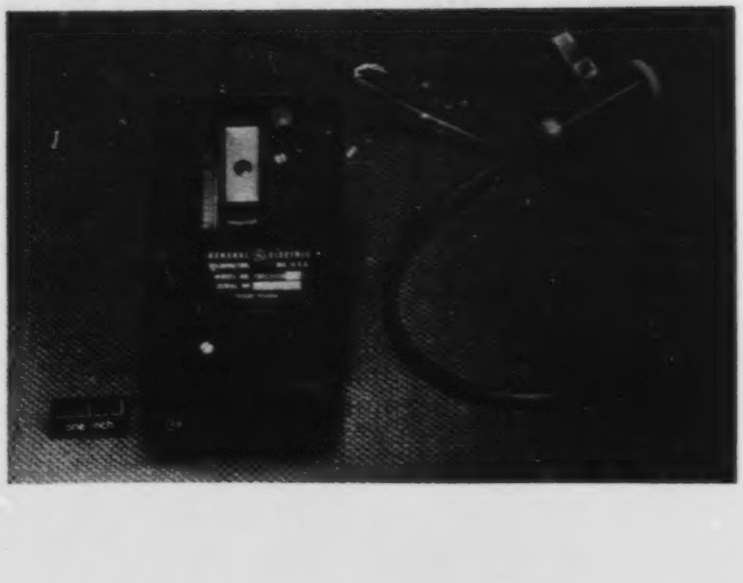

FIGURE 8. Carbon monoxide dosimeter, rear view.

but can be modified by factory adjustment. A self-test circuit is available for the alarms, so that when the unit is turned on the alarms will illuminate/ buzz for approximately 15 seconds to advise that the alarms are functioning.

The dosimeter unit has all of its adjustment controls recessed in the face of the unit and covered by a key-locked door. This feature is provided to minimize the possibility of the worker tampering with the controls during operation. Visible to the worker (on the rear of the unit, Figure 8) are windows showing the level of distilled water in the cell, and a rotameter showing the pump speed (and that the pump is working). A pump speed adjust pot is also located on the rear of the case.

Controls and adjustment points for the personal dosimeter are shown in Figure 9. Behind the keyed door of the dosimeter are the battery and pump on/off switches, the zero and span adjust screws, and the cable connection for readout of the coulometer at the support console and charging of the battery. Both a gas sample inlet port and a distilled water fill port are available on top of the dosimeter case.

Support Console

A support console (6 in wide x 6 in high x 6 in deep) is required in conjunction with the personal dosimeter and can also be used with the direct reading detector. The console digitally displays the total cumulative carbon monoxide dosage during the prescribed operating period. The console also provides a digital display of the instantaneous carbon monoxide level when used in conjunction with the dosimeter. This latter display is used for calibration of the dosimeter, as shown in Figure 10.

The support console also provides a battery charging capability for the dosimeter. A single and six dosimeter charging support console (Figure 11) is available. The multiple charge support console also has the capability of testing the state of the battery charge, and it has a jack plug for use with a external recorder.

Maintenance

A table of maintenance recommendations for the detector and dosimeter units are presented in Table 4.

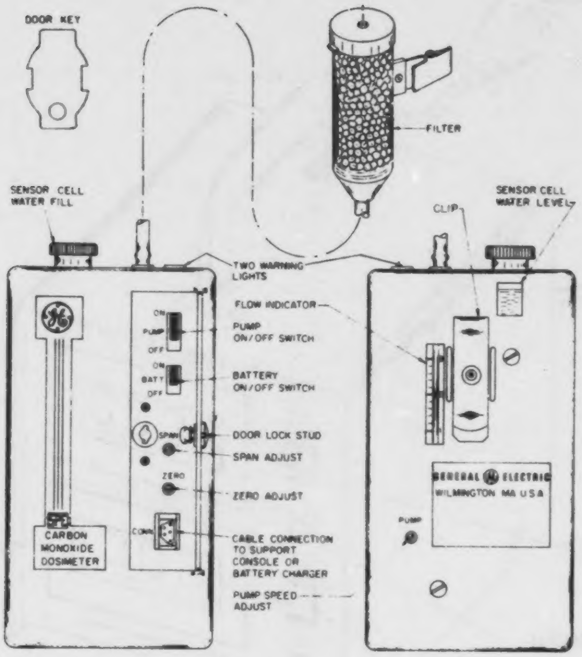
DOOR KEY
FILTER
SENSOR CELL WATER FILL
SENSOR CELL WATER LEVEL
CLIP
TWO WARNING LIGHTS
FLOW INDICATOR
ON
PUMP
OFF
PUMP ON/OFF SWITCH
ON
BATT
OFF
BATTERY ON/OFF SWITCH
SPAN
DOOR LOCK STUD
SPAN ADJUST
ZERO
ZERO ADJUST
CONN
CABLE CONNECTION TO SUPPORT CONSOLE OR BATTERY CHARGER
PUMP SPEED ADJUST
CARBON MONOXIDE DOSIMETER
GENERAL ELECTRIC
WILMINGTON MA USA
PUMP

FIGURE 9. CO dosimeter controls and adjustment points.

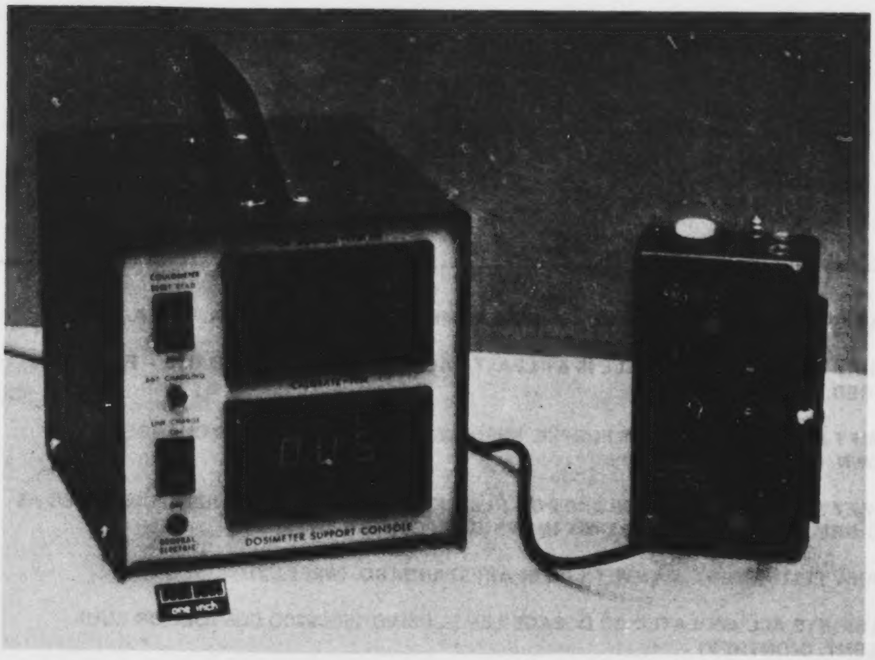
DOSIMETER SUPPORT CONSOLE
one inch

FIGURE 10. Dosimeter and support console.

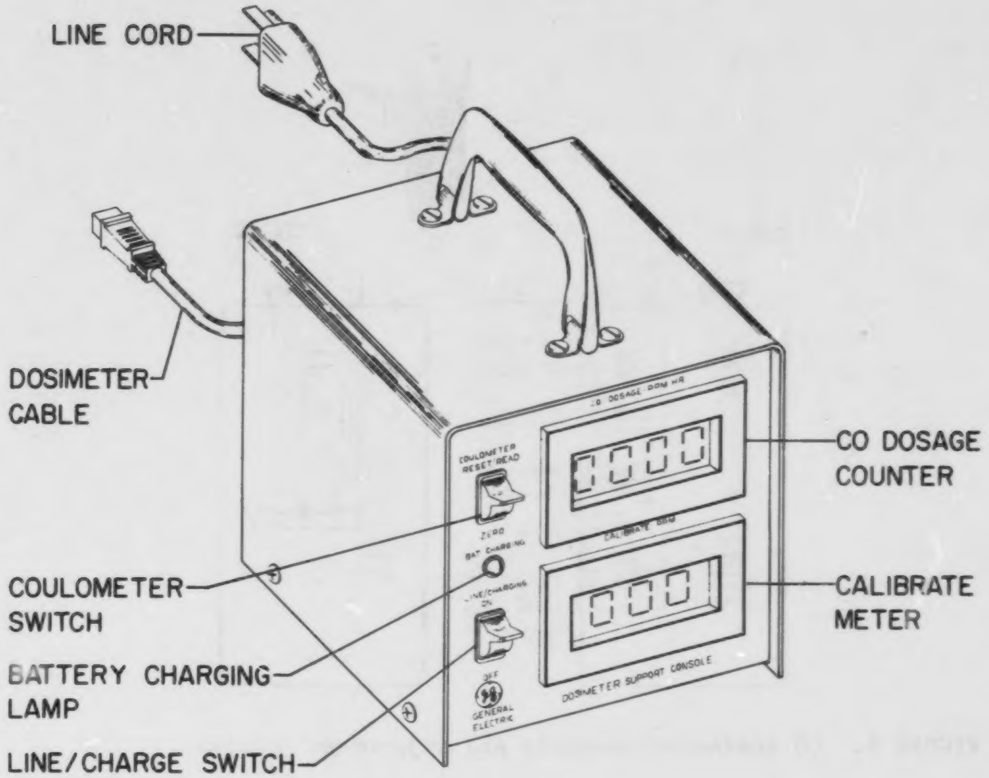
LINE CORD
DOSIMETER CABLE
CO DOSAGE PPM HR
COULOMETER RESET/READ
ZERO
BAT CHARGING
LINE/CHARGING ON
OFF
GENERAL ELECTRIC
CALIBRATE PPM
DOSIMETER SUPPORT CONSOLE
CO DOSAGE COUNTER
COULOMETER SWITCH
BATTERY CHARGING LAMP
CALIBRATE METER
LINE/CHARGE SWITCH

FIGURE 11. A single and six dosimeter charging support console.

TABLE 4

Function and Maintenance

CHARGE NI/CD CELLS FOR 14 HOURS AT A NOMINAL CURRENT = 30 mA. ± 3 mA. (DAILY)

VERIFY WATER LEVEL IN CELL IS AT LEAST HALF FULL OF DISTILLED H_2O – FILL AS REQUIRED. (WEEKLY)

VERIFY FILTER MATERIAL IS PURPLE. REPLACE FILTER WHEN COLOR CHANGES TO BROWN. (WEEKLY)

VERIFY SAMPLE AIR FLOW OF 2±0.2 ON FLOW INDICATOR SCALE. ADJUST PUMP SPEED AS REQUIRED WITH HAND-HELD UNIT IN UPRIGHT POSITION. (WEEKLY)

VERIFY INSTRUMENT SPAN WITH CO IN AIR STANDARD. (WEEKLY)

CALIBRATE ACCUMULATED CO DOSAGE LEVEL USING 15ECS2CO CONSOLE OR EQUIVALENT. (MONTHLY)

EMPTY CELL WATER RESERVOIR AND REFILL WITH FRESH DISTILLED WATER. (MONTHLY)

OPERATIONAL TEST RESULTS

Typical results of operational testing of the dosimeter and detector units are presented in the next series of figures.

Response versus Concentration

The indicated response of the units to various concentrations of CO in air (at 60 cc/min pump rate, 24° C) are shown in Figure 12. The data follow the linear response curve anticipated over the entire 0 to 1,000-ppm range of concentration.

Response versus Time

The indicated response of a specific CO detector unit to CO gas concentrations at various time intervals is shown in Figure 13. In these tests, three different CO concentrations (97 ppm, 460 ppm, and 1,040 ppm) were separately fed to the instrument for 200 sec (at 60 cc/min, 24° C). At the end of 200 sec, CO-free air was fed to the instrument. The response time obtained lies well within the specified response time.

Response versus Temperature

The indicated response of dosimeter and detector units to various concentrations of CO (21, 58, and 97 ppm) at different temperatures is shown in Figure 14. In these tests, the sensing instrument was left at the specified temperature a minimum of 60 minutes prior to obtaining the reading. The results obtained are within specifications established for the instrumentation.

Response versus Flow Rate

The indicated response of the detector to variations in sample flow rate with 97 ppm CO calibration gas, after calibration at 60 cc/min and 24° C, is shown in Figure 15. The results show some sensitivity of output response to flow rate change. The pump is, however, extremely stable in operation and will maintain the pump rate within ± 2 percent in normal daily operation. Variations encountered as a result of normal flow rate changes lie well within the specifications established for instrumentation.

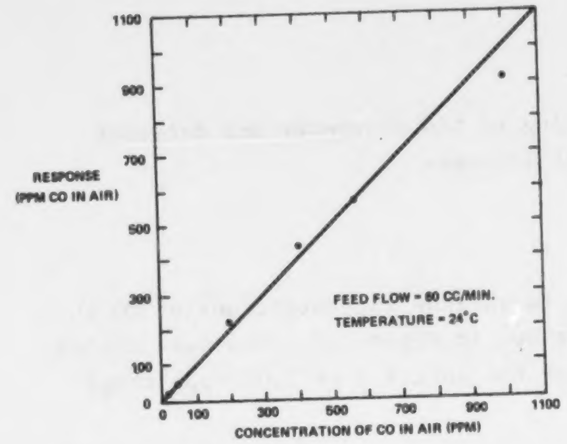

FIGURE 12. Response versus concentration for a General Electric portable CO detection instrument.

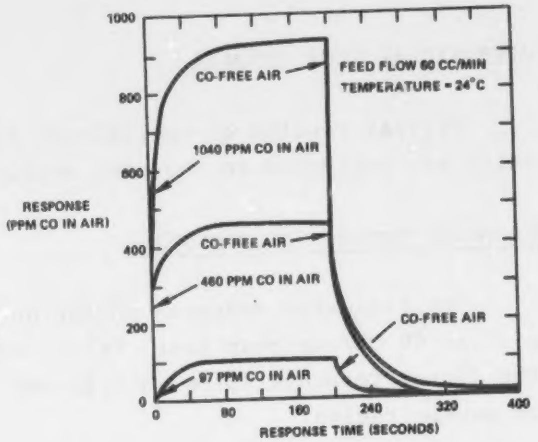

FIGURE 13. Response versus time for a General Electric portable CO detector to CO in air feeds.

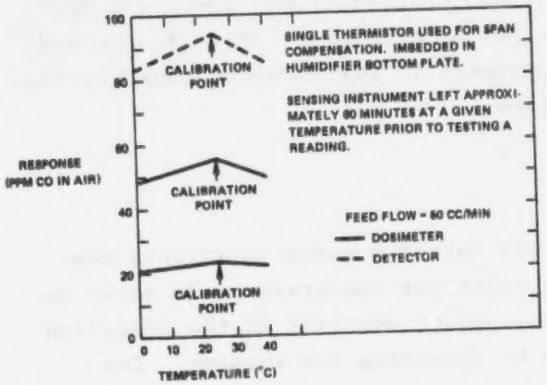

FIGURE 14. Response versus temperature (° C) for General Electric CO gas detection instruments.

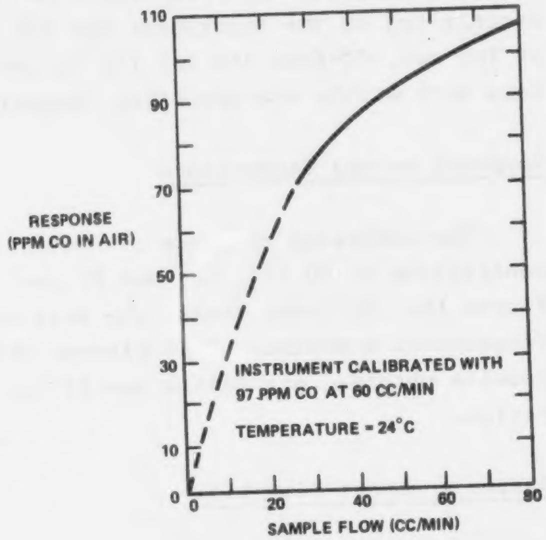

FIGURE 15. Effect of flow on response for a General Electric CO detection instrument.

CONCLUSION

A new family of miniaturized self-contained carbon monoxide dosimeters and direct reading detectors have been described. The units are extremely lightweight, versatile, self-contained, and meet the requirements for intrinsically safe operation. The cell needs no acid; only distilled water is required. The units are an outstanding example of the combination of functional design engineering and technical experience based on fuel cell technology.

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Discussion

ZISKIND: Richard Ziskind, Science Applications. How much field experience has been accumulated on this instrument?

GRUBER: The dosimeter has been in the field for well over a year. The detector is being introduced at this point in time. The circuitry and design of both the detector and the dosimeter are quite similar.

Before we introduced the product, we at GE did considerable testing of the product, both in-house and with some field testing as well. Both units have been tested for at least 2 years, the detector being tested for at least 1 year prior to its introduction.

ZISKIND: The other question I had was the question that was asked before about electromagnetic interference.

GRUBER: As a matter of fact, the unit also has a plastic case. The plastic case is metalized. One of our specifications is no electromagnetic interference, and the units will meet that specification.

WILLIAMS: Marsha Williams. To what extent has the instrument been tested at temperatures below zero Centigrade?

GRUBER: As with some of the other electrochemical cells used below zero, we have a water cell. The water will freeze, and you can deteriorate your cell at low temperatures. This is the same with all of the electrochemical cells.

All of the electrochemical cells have specific temperatures to which they can go down. Regarding a water cell, obviously you wouldn't want to go below zero degrees Centigrade. With some of the acid cells--they can go down below zero Centigrade.

MEIER: Could you say something about cost?

GRUBER: Vic Socol, would you like to say a couple of words?

SOCOL: The dosimeter costs $595. There are various options on the support console, which cost from $695 to $825, and a direct reading indicator, at $945.

McSTRAVICK: John McStravick, Energetics Science. Just for the record, the current Energetics Science dosimeter sensor can go to -17° Centigrade.

Design and Performance of a Reliable Personal Monitoring System for Respirable Particulates

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Steven D. Colome
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INTRODUCTION

Personal exposure to respirable particulates and sulfates is being measured as a part of a long-term prospective epidemiological study of the respiratory health effects of air pollution, the Harvard Six City Study (1). The purpose of this monitoring program is to develop better estimators of actual personal exposure from comparison of the direct measurements of personal exposure with simultaneous measurements of the normally measured outdoor air, the air inside each participant's home, and records of the daily activities of each participant. Results are reported elsewhere in these Proceedings (2).

Respirable particulates and sulfates were selected for monitoring because they were considered to be important potential toxic agents. Furthermore, for practical considerations, reliable sampling equipment which modeled the definition of "respirable particulates" (3) was commercially available and readily adaptable for use in the community.

The commercially available samplers have been designed to meet Federal requirements for respirable dust exposures in mines (4). In this program, MSA Model G and Bendix BDX-31 samplers were used. The sampler consists of a 10-mm nylon cyclone presampler to remove the nonrespirable particles, followed by a filter to collect the respirable fraction. Air is drawn through the sampler by a battery-operated diaphragm pump which is equipped with a stroke counter and miniature rotameter. The pump is designed to operate from the batteries for a normal 8-hour work shift. Flow is controlled by a needle valve. Normal operation calls for overnight charging of the batteries. At the beginning of the sample, the pump is turned on and allowed to run for approximately 15 minutes to eliminate initial battery voltage surge before setting the flow to 1.7 liters-per-minute (lpm). At the end of the sample, the flow is checked and the total number of strokes recorded as an indication of total sample volume.

In applying these samplers in the community, the first problem we encountered was unacceptable noise. The situation was somewhat improved by placing the pump in a hard plastic box lined with sound-absorbing material. The box was equipped with a shoulder strap, and the cyclone was mounted on the outside of the box. Problems arose with sampling lines being crimped within the box with this setup.

The second major problem was with the limited sampling time. A sampling time of 24 hours was desired for comparison with regular State and Federal air pollution sampling programs, and also to ensure sufficient collected mass for analysis. Given a nominal battery life of 8 hours, a supplementary power source was required. The battery chargers operate in two modes--16-hour and 64-hour recharging. At the high rate, 16 hours, the chargers supply enough power so that there is only a slight drain on the batteries. Thus, the participants were instructed to place the monitor in some fixed location whenever they were in a room for some extended period--for example, on their desk while working in their offices. The charger was then plugged into 120 VAC outlet and then into the pump.

This procedure proved to be less than ideal. The pumps were still noisy. The chargers were bulky and inconvenient to carry around. In the first sampler program in Watertown, Mass., 37 people agreed to participate. Thirteen did not last through the first sampling day. In the end only 18 highly motivated people remained. In addition, we encountered several electrical problems. First, if the MSA chargers were plugged in while the pumps were operating and the charger was on, they blew their internal fuse. Secondly, the higher voltage supplied by the chargers quickly deteriorated the motor brushes, and we had a very short motor life. The charger connected to the pump was not secure so that the plug often slipped out without the participant's knowing it.

The final problem was variation in the flow rate. The actual flow was proportional to the voltage supplied to the motor. Since even with the chargers attached, the pumps still drew power from the batteries, the flow declined during the day as the battery voltage decayed. On the average, the end flow was 80 percent of the nominal initial setting.

The commercial samplers were modified at several steps along the way, but it was readily apparent that these samplers were not acceptable for our program. As a result, the Harvard/EPRI sampler was developed.

The design criteria were:

1) Provide a constant flow rate of ± 0.1 liter-per-minute (lpm) over the range of 0.5 to 3.0 lpm;

2) Include the self-contained capability to be recharged overnight and/or to run off line voltage;

3) Produce a noise level acceptable for home and office use;

4) Operate for 12 hours or more on batteries;

5) Portable, lightweight, rugged, yet simple to operate;

6) Provide a sample comparable to our fixed-location indoor/outdoor monitoring system; i.e., system operating where no pulsation is present.

One hundred personal monitoring pumps have been built and have passed initial testing. They are presently being field tested and will be put into full use during a personal monitoring program during the spring of 1979.

SPECIFICATIONS

Size: 6 in x 6 in x 3 in
Weight: 4 lb
Pump: "Brailsford" Brushless TD-3LL or TD-3L
Battery Pack: "Gould" 12 V-1.2 SC cells Ni-Cad
Flow Control: Variable Constant Voltage
Range of Operation: 0.5 to 3.0 lpm
Case Metal: Aluminum
Cyclonic Separator: 10-mm nylon with filter
Features:

- Self-contained battery charger
- No warm-up time required to reach stable flow
- 14 to 20 hours sample time on battery mode, indefinite from line voltage
- Minimum maintenance brushless pump (10,000 hours before service)
- Quiet operation.

PRINCIPLE OF OPERATION

Air is drawn through the 10-mm nylon cyclone, a 1.0 µ pore size Fluoropore filter, and a pulsation damper by a constant displacement pump (Figure 1). The flow control through the system is controlled by varying the speed of the pump instead of by conventional throttling methods. This allows for precise flow control with minimum energy loss due to pumping losses induced by throttling. The variable constant voltage power supply allows the pump to be set at a given flow rate and will maintain the flow ± .05 lpm under normal sampling loads and ± .1 lpm under severe filter loading conditions.

The Harvard/EPRI sampler has a six-position switch as follows:

1) Battery Run
2) Line Run
3) Line Run and Charge Low
4) Charge Low (36 to 40 hours)
5) Charge High (12 to 14 hours)
6) Off.

These six positions allow the unit to serve as a portable personal monitoring device or a stationary 24-hour sampling unit. The unit has a detachable 8-foot, three-wire safety power cord and a detachable 48-inch carrying strap. The respirable sampling cassette and cyclonic separator can be detached and located apart from the main body of the sampler.

RESULTS OF FIELD TESTING

Flow Stability

Laboratory and field tests conducted between October and December of 1978 have shown the flow to be stable to ± .05 lpm under normal filter loadings for 12 to 24 hours, after an initial break-in period for each unit (72 hours). This break-in period is required to seal the pump valves and to establish a diaphragm set. On some units it has been necessary to install a restricting orifice in line to allow the pump to obtain lower flow rates. This does not affect the stability or designed sampling life times while operating from batteries.

Effects of Pulsation on Cyclone Efficiency

The effects of air flow pulsation on the cyclone collection efficiency in personal sampling devices have been investigated by numerous researchers

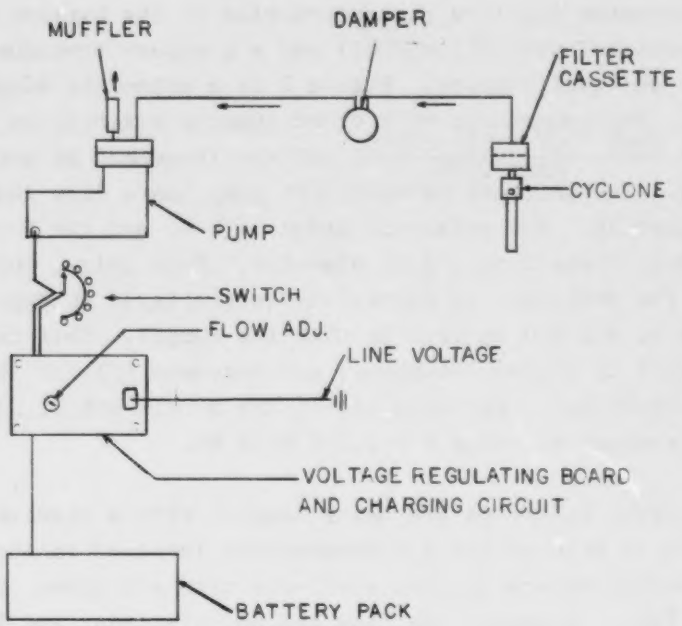
MUFFLER
DAMPER
FILTER CASSETTE
CYCLONE
PUMP
SWITCH
FLOW ADJ.
LINE VOLTAGE
VOLTAGE REGULATING BOARD AND CHARGING CIRCUIT
BATTERY PACK

FIGURE 1. Schematic of flow system.

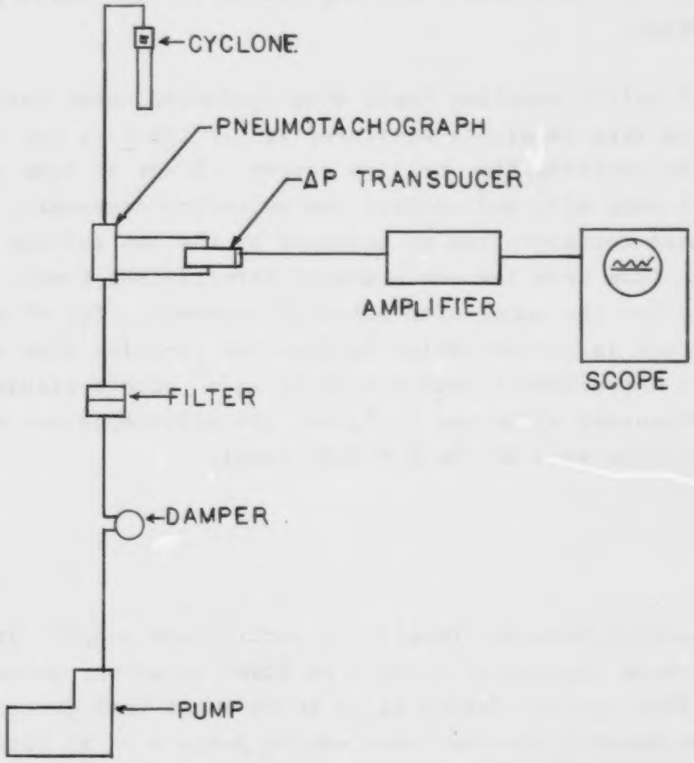
CYCLONE
PNEUMOTACHOGRAPH
ΔP TRANSDUCER
AMPLIFIER
SCOPE
FILTER
DAMPER
PUMP

FIGURE 2. Test apparatus.

(5,6,7). To determine the flow characteristics of the Harvard/EPRI pump, a Fleisch Pneumotachograph (#7316[000]) and a pressure transducer were coupled to an amplifier and oscilloscope. Figure 2 is a schematic display of the test apparatus. For comparison with other pumping systems, an index of pulsation $(P = \frac{[\text{MAX FLOW} - \text{MIN FLOW}]}{\text{MEAN FLOW}})$ and the frequency of oscillation were determined. The undamped Harvard/EPRI pump has a flow characteristic as shown in Figure 3A. The pulsation index is 6.0, and the frequency of cycling is 62.5 Hz. Installing a 3-cm diameter, .8-cm thick, rubber pulsation damper reduced the amplitude of pulsation, as displayed in Figure 3B. This pulsation index is now 2.0 at 62.5 Hz with the damper. This is comparable to values reported by Caplan, Dougheny, and Sorensen (5) for the MSA Model G pump (P = 2.5 @ 38 Hz). For comparison, the Bendix BDX 31 flow characteristics were determined as being P = 1.0 @ 46.3 Hz.

Respirable size particles are being sampled with a network of indoor/outdoor samplers in each of the six communities involved in the epidemiologic study. These particles are sampled similarly with a cyclone preseparator and a Teflon filter. However, the flow has no pulsations and is controlled by a limiting orifice. It is important that respirable particle and sulfate data collected in the personal monitoring system be equivalent to the fixed-location monitoring.

A series of paired sampling tests were conducted under various mass loadings. Flow rates were carefully monitored at 1.7 lpm ± .1 for both the Harvard/EPRI pump and the limiting flow orifice system. A set of runs was made for the Harvard/EPRI pump with and without the pulsation dampeners. The mean difference in mass concentration as measured by the two systems was significantly different from zero for the undamped Harvard/EPRI pumps, and not different from zero for the pumps with pulsation dampers. For 40 paired samples, the mean difference in concentration between the limiting flow orifice and pulsation-damped Harvard/EPRI pump was $-0.28\ \mu g/m^3$ with a standard deviation of 13.0. The r-squared value was 97.9, and the difference was not significantly different from zero at the P = 0.05 level.

CONCLUSIONS

The Harvard/EPRI personal respirable particulate sampler is a reliable system that provides comparable results to fixed-location, pulsation-free samplers. The flow control design is an improvement that provides assurance that sample flow remains constant over sample periods of at least 12 hours.

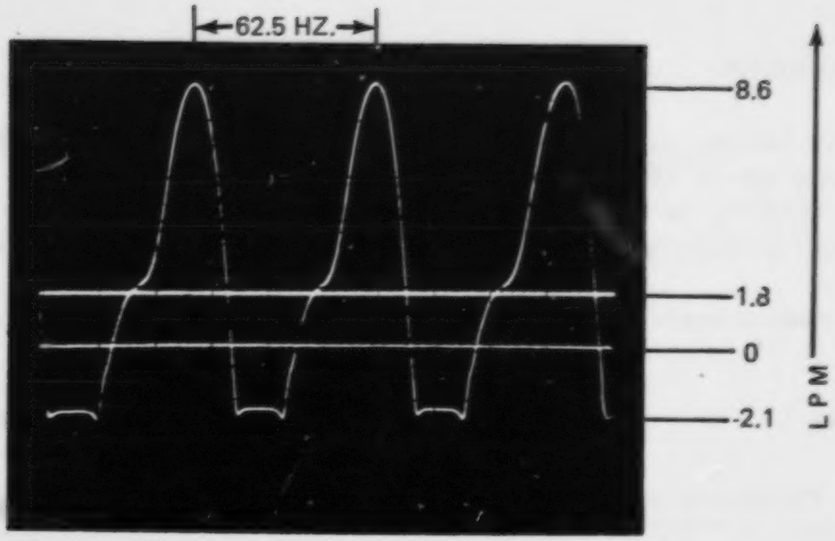

FIGURE 3A. H/E without damper.

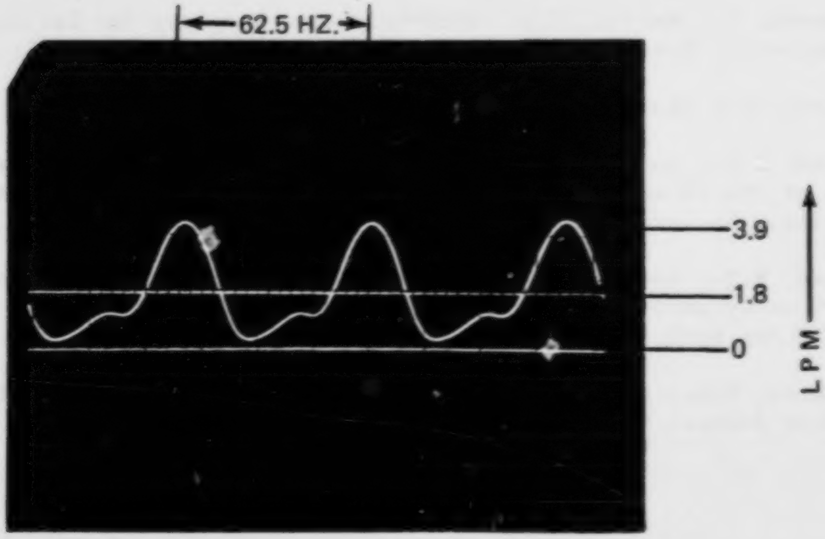

FIGURE 3B. H/E with damper.

In addition, the self-contained charging circuitry and lower noise level have eliminated the nuisance characteristics that prevented broader participant acceptance. The Harvard/EPRI pump has been designed to meet the particular sampling requirements of assessing community personal exposures in an epidemiologic air pollution health study.

ACKNOWLEDGEMENTS

Steve LeMott, Harvard School of Public Health, Department of Physiology, for aid and use of the pulsation measurement equipment.

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Discussion

(NOTE: The discussion for this paper appears following the text of the next paper, "Personal Exposure to Respirable Particulates and Sulfates: Measurement and Prediction.")

Personal Exposure to Respirable Particulates and Sulfates: Measurement and Prediction

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INTRODUCTION

Epidemiological studies of the health effects of air pollutants have in the past frequently depended on ambient air quality measurements at a single site within a community for correlation with observed health effects. Given that Americans normally spend 95 percent of their time indoors (1,2), such measurements of outdoor air pollution levels may not represent the actual air pollution exposure of the sample population.

Jackson and Newill (3) noted that "perhaps the weakest link in our attempts to establish the exposure-response relationship is in obtaining an accurate quantitative estimate of exposure." Morgan and Morris (4), in a study of the needs for personal monitoring, concluded that "the importance of population exposure measurements in air pollution epidemiology makes it imperative that future epidemiological studies include exposure estimates more representative of what people actually breathe."

A monitoring program to measure personal exposure to respirable particulates and sulfates was undertaken as part of a long-term epidemiologic study of the respiratory effects of air pollution (5). These observations were compared to measurements of the ambient outdoor environment and of the indoor environment in each participant's home. In a similar study, Binder et al. (6) had 20 school children carry a suitcase sampler with them for 1 day. They concluded that outdoor measurements do not accurately reflect the particulate exposure of individuals who live in the area of sampling.

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With observations of actual personal exposure to respirable particulates, we hope to develop a method to characterize the personal air pollution exposure of individuals in terms of their personal activities, characteristics of their home and household, and ambient pollution level. Average exposure can be estimated by a simple time-weighted model of the form

$$\overline{C} = \sum_i t_i c_i \Big/ \sum_i t_i$$

where $\overline{C}$ is the average exposure, t_i is the time spent in activity i, and c_i is the air pollution concentration associated with that activity.

Ideally, the air pollution concentration associated with each activity would be known, so that the exposure of any individual could be estimated directly from his or her activities. It is unrealistic to expect that we can specify air pollution concentrations for every activity, but hopefully we can make reasonable estimates for broad classes of activities. While not specifying exposure exactly, these estimates should be significantly better than the outdoor values alone.

The method used, therefore, was to measure the integrated exposure of individuals with different activity patterns. Comparison with simultaneous measurements outside and inside their homes allowed the most important factors in determining exposure to be identified and quantified.

PROCEDURE

Volunteers were asked to carry a small, personal particulate monitor with them for 24 hours as they went about their normal daily activities. They were also asked to keep a diary of their activities that day. Similar monitors were run concurrently at fixed sites in their home and at several locations outside in the community. Samples were taken in Watertown, Mass., every 6th day for 2 months in the summer (July and August 1975) and 2 months in the winter (mid-January to mid-March 1976). The study was repeated in Steubenville, Ohio, in June 1976. In this case, 12-hour samples were taken on Monday, Wednesday, and Friday each week.

Volunteer Selection

Volunteers were solicited at random from census lists. The study was described to the potential participants in a letter followed by a phone call.

Those interested in the study were visited and shown the equipment. Although the intent was to draw a representative sample of the population, this did not occur. In general, anyone doing physical work could not conveniently carry the monitor. Most working people with manufacturing jobs were not allowed to bring the monitors to work by their employers for fear that they would uncover occupational health violations. Many potential participants found the program too burdensome. The final set of volunteers provides a very wide range of exposures and activities, but was not representative of the sample population in the health study.

Whenever possible, we attempted to have both the husband and wife in a family participate. A total of 37 people participated, 18 in Watertown and 19 in Steubenville. There were five smokers in the Watertown sample, and one in the Steubenville sample. Twenty-one of the participants were women, and 23 were employed away from home. All those working had white collar jobs except for one self-employed plumber.

Pollutant Measurements

In order to characterize those particulates which are most likely to have a significant respiratory health effect, we chose to measure only those small enough to penetrate deep into the lungs. The AEC Los Alamos criteria (7)--which specify that 50 percent of the 3.5-μm particles penetrate deep into the lungs, while particles larger than 10 μm will not--was used. This also provides a convenient starting point for measuring individual exposure to air pollution in the community in that sampling devices had been developed for the industrial environment based upon these criteria.

The sampler consists of a Dorr-Oliver 10-mm diameter hydroclone presampler, followed by a 37-mm Fluoropore filter with a 1-μm pore size. Air is drawn through the sampler by a Mine Safety Appliance Portable Pump--Model G was used in Watertown, and a Bendix BDX Super Sampler in Steubenville. A flow rate of 1.8 liters-per-minute has been shown by Seltzer, Bernaski, and Lynch (8) to deposit particulates in the cyclone presampler in close approximation to the Los Alamos curve. This was the flow used in this sampling. The American Industrial Hygiene Association (9) has recommended a flow of 1.7 liters-per-minute (lpm) for the 10-μm cyclone. Knight and Lichti (10) have shown essentially no change in the mass collected on the filter between 1.3 and 2.65 lpm. It is felt, therefore, that this difference in flow rate does not compromise the samples.

The pumps are battery-operated, with a nominal operating time of 8 hours.

It was possible to operate the pumps for longer periods by connecting them to their battery chargers with only a small drain on the batteries. Since initial tests showed that the major obstacle for people participating in the study was the noise of the pump, the pump was placed in a sound-insulated box with a strap so that the monitor could be carried over the shoulder, as shown in Figure 1.

Sampling Plan

In Watertown, samples were collected for 24-hour periods every 6th day to coincide with Federal and State air quality sampling programs. In Steubenville, 12-hour samples were taken on Monday, Wednesday, and Friday, beginning at 8 a.m. At that time, the volunteer turned on his personal monitor and a similar one placed in the home in the room with the most activity (excluding the kitchen). At the same time, outside monitors were turned on by automatic timers. Thus, we had three measurements for each sample--personal, inside the home, and outside.

We assumed that the particulates were uniformly distributed over volumes the size of a room. The actual placement of the monitor on the person was therefore not critical, and breathing zone samples as required in industry were not necessary. Volunteers were instructed to connect the pumps to the chargers whenever they were in one area for an extended period. In this way, we were able, in most cases, to run the samplers for up to 24 hours. (This type of operation is not recommended by the manufacturer.) The volunteers were also asked to keep a diary of their activities during the sampling period, including how many cigarettes they were exposed to each hour.

Outdoor monitors were located throughout the community. The outdoor monitoring was part of a continuing program to evaluate the indoor/outdoor pollution relationships. The outdoor data were pooled to give the mean outdoor value for each day with observations. Hereafter, this pooled outdoor mean will be referred to as the "outdoor concentration." This is the concentration which would be obtained by an ambient air pollution monitoring site using this sampling technique.

Sample Analysis

Filters were preweighed on a Cahn 4100 Electro-Balance in a humidity-controlled room (RH <50 percent) and sealed in plastic sampling cassettes. The volunteer was visited after each sampling day, the filters were changed, and the operation of the pump was checked. Flows were checked periodically,

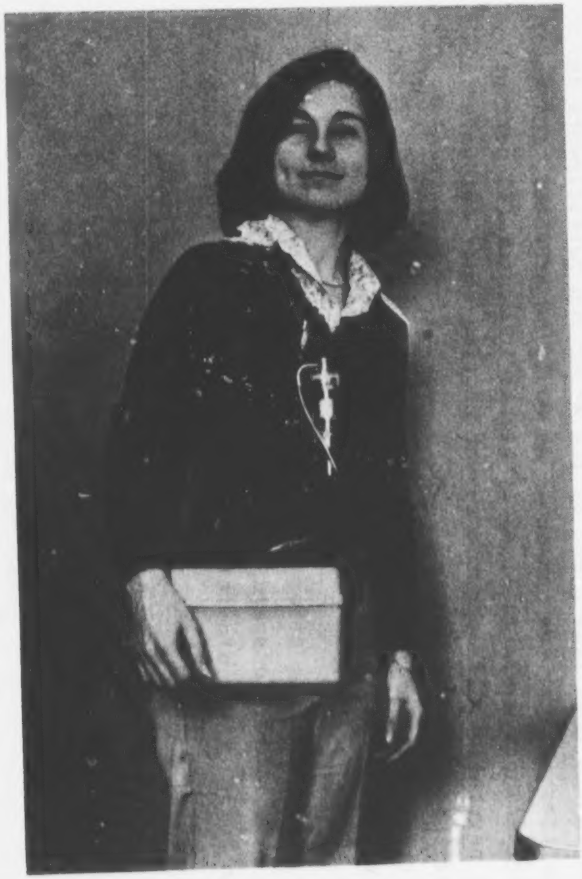
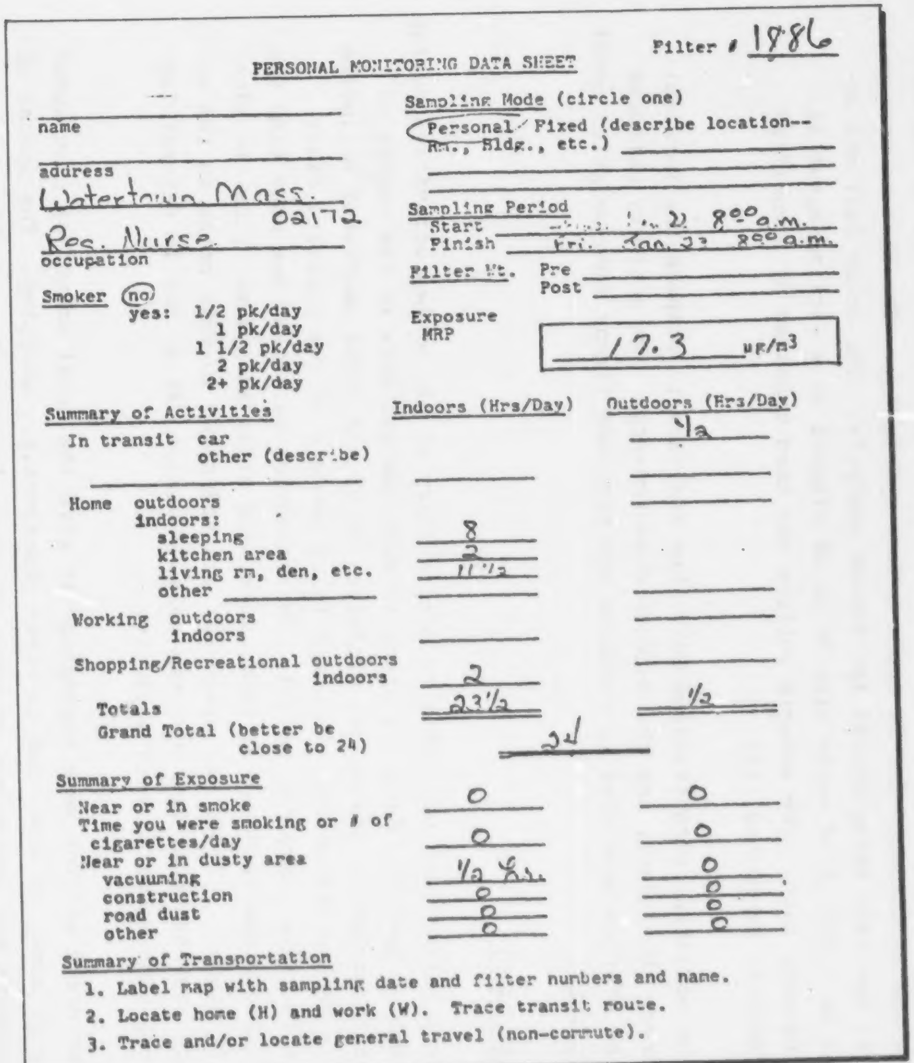


FIGURE 1. Personal respirable particulate monitor showing sound deadening box and normal carrying mode.



Filter # 1886

PERSONAL MONITORING DATA SHEET

name ______________

address
Watertown Mass.
02172

Res. Nurse
occupation

Smoker [✓ no]
yes: 1/2 pk/day
1 pk/day
1 1/2 pk/day
2 pk/day
2+ pk/day

Sampling Mode (circle one)
[✓ Personal] / Fixed (describe location--Rm., Bldg., etc.) ______________

Sampling Period
Start [illegible] 22 8^{00} a.m.
Finish Fri. Jan. 23 8^{00} a.m.

Filter Wt. Pre ______
Post ______

Exposure
MRP 17.3 μg/m³

Summary of Activities		Indoors (Hrs/Day)	Outdoors (Hrs/Day)
In transit	car		1/2
	other (describe)		
Home	outdoors		
	indoors:		
	sleeping	8	
	kitchen area	2	
	living rm, den, etc.	11 1/2	
	other		
Working	outdoors		
	indoors		
Shopping/Recreational	outdoors		
	indoors	2	
Totals		23 1/2	1/2
Grand Total (better be close to 24)		24	

Summary of Exposure		
Near or in smoke	0	0
Time you were smoking or # of cigarettes/day	0	0
Near or in dusty area		
vacuuming	1/2 hr.	0
construction	0	0
road dust	0	0
other	0	0

Summary of Transportation

1. Label map with sampling date and filter numbers and name.
2. Locate home (H) and work (W). Trace transit route.
3. Trace and/or locate general travel (non-commute).

FIGURE 2. Example of personal monitoring data sheet used in 1976 winter sample.

but not after each sampling day. The used filters were returned to the laboratory and conditioned for 24 hours before reweighing. The filters were cut in half, one half being stored for future analysis. The other half was extracted in 1,100 µl of water with 50 µl of ethanol as a wetting agent in an ultrasonic bath. The soluble sulfate was then measured by a modified turbidimetric technique (11).

The measured concentrations were then analyzed to compare the personal exposures, the indoor, and the outdoor measurements. The activity patterns from the diaries were used to evaluate the proposed linear time-weighted model for exposure.

Activity Diary

Each participant was asked to keep a diary of his or her activities during the sampling period. Each was asked to make special note of the number of cigarettes smoked in his or her vicinity, or of any other source of pollution of which he/she was aware. Figure 2 is an example of the activity diary used in the first sampling period. The volunteer was asked how much time was spent indoors and outdoors at home, work, and other locations, plus the time spent in transit. There was space for the volunteer to make notes on the activities hour by hour, but this was only to assist him or her in determining the total time spent in each activity.

The diary entries were aggregated to give the total amount of time spent indoors at home, at work, and in other places--e.g., shopping. The amount of time outdoors was determined at home, at work, in transit, and all other places. Table 1 shows the mean time spent by the Watertown participants in each of these activities for the two seasons. As would be expected, the total amount of time spent indoors was significantly higher in winter (95 percent) than in summer (86 percent). Although the amount of time spent outdoors in winter is about one-third that of summer, in both seasons an average of 1 hour was spent in transit; that is, traveling by auto, public transportation, foot, or some other method.

These results are similar to other time-usage studies (1), which have shown people in 44 U.S. cities to spend 94.5 percent of their time indoors--70.9 percent in the home. These studies also found that an average of 1.25 hours per day were spent in transit.

TABLE 1
Mean Daily Time Spent in Various Activities for 18 Participants in Watertown, Mass.

Location	Summer Mean	Summer (SD)*	Summer %	Winter Mean	Winter (SD)*	Winter %
Indoors						
Home	16.8	(6.5)	71.9	18.2	(6.4)	78.5
Work	2.6	(3.9)	11.1	2.8	(4.7)	12.0
Other	0.6	(1.8)	2.6	1.0	(2.1)	4.2
Total Indoors	20.0	(5.9)	85.6	21.9	(4.3)	94.8
Outdoors						
Home	1.7	(4.7)	7.3	0.0	(0.3)	0.2
Work	0.1	(0.3)	0.2	0.1	(0.9)	0.4
Transit	1.0	(1.2)	4.1	1.0	(1.2)	4.2
Other	0.7	(1.8)	2.9	0.1	(0.5)	0.5
Total Outdoors	3.4	(4.9)	14.5	1.2	(1.5)	5.2
Total All	23.4		100	23.1		100

*SD = Standard Deviation

One volunteer in Watertown attempted to evaluate the relative impacts of different modes of transportation. One day, he took his car to work. The next sampling day, he bicycled. The third day, he canoed down the Charles River. Unfortunately, any differences which might have existed were masked by the high particulate levels from his smoking.

RESULTS

In Watertown, a total of 287 personal and 251 indoor samples were collected. Over half the potential samples were missing because of equipment problems, vacations of the participants, voided observations, and scheduling problems. In Steubenville, 245 personal and 131 indoor samples were collected. The data-retrieval rate there was higher because of the shorter sampling time and closer supervision.

Sulfate Relationships

There are two questions to be answered from this data. First, is personal exposure related to the normally monitored outdoor air pollution levels? Secondly, if not, what is the best estimator of personal exposure, and what is the minimum information required for that estimate?

We will consider only comparisons of mean levels for each individual in the study. Observations are included only when we have a complete set of personal, indoor, and outdoor measurements of concentration for that individual and that day. While cutting down the number of available observations, this ensures comparability. We will also require each individual to have at least three complete sets of observations in order to be included.

Consider the respirable sulfates first. Although sulfate particulates are generated by matches (12) and the open burners of gas stoves (13), the contribution is small compared to the concentrations of sulfate in the outdoor air in Watertown and Steubenville. We can then easily explore the relationship between personal exposure and outdoor concentration. In Figure 3, mean personal exposure levels are plotted against the mean matched outdoor concentration for each individual. The points are clustered into two groups: Watertown observations with the lower values (mean outdoor = 5.8 $\mu g/m^3$), versus Steubenville observations with higher values (mean outdoor = 17.6 $\mu g/m^3$).

The correlation coefficient (r) between the outdoor and personal means is 0.81, but from visual inspection it is clear that the outdoor means are not good estimators of personal exposure. There is considerable scatter, especially in Steubenville, about the perfect prediction line, the diagonal in Figure 3. The proportion of the variance of the mean personal exposures explained by a linear regression on mean outdoor concentrations (r^2) is 65 percent. But considering the mean outdoor values to be a direct estimate of personal exposure, a more appropriate statistic is the standard error about that estimate, which is 4.86 $\mu g/m^3$.

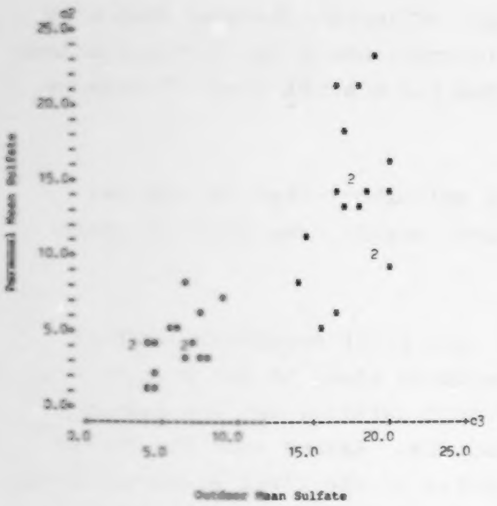


FIGURE 3. Relationship between mean outdoor and mean personal sulfate levels ($\mu g/m^3$).

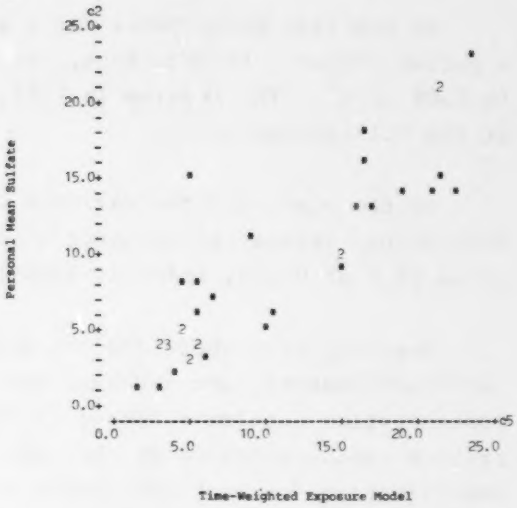


FIGURE 4. Relationship between measured personal mean sulfate levels ($\mu g/m^3$) and predicted personal mean sulfate levels from time-weighted exposure model.

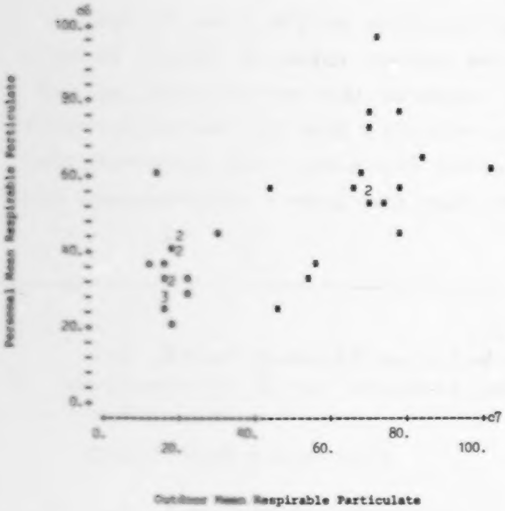


FIGURE 5. Relationship between personal mean and outdoor mean respirable particulate levels ($\mu g/m^3$).

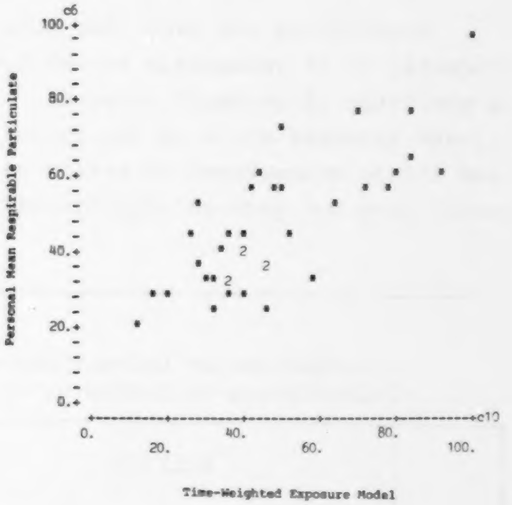


FIGURE 6. Relationship between measured personal mean respirable particulate levels ($\mu g/m^3$) and predicted personal mean respirable particulate levels from time-weighted exposure model.

We can test these pairs for a significant difference between them with a paired t-test. In this case, the mean difference among the 37 observations is 3.06 $\mu g/m^3$. The t value is 4.87, which implies a significant difference at the 0.1-percent level.

We can also test the variance about the estimator--that is, the outdoor means--versus the variance of the personal means. The ratio of these gives an F of 0.625, which is significant.

Assuming that there are no significant sources of respirable sulfate particles indoors, the personal exposure should be equal to the mean of the concentration outside weighted by the time spent outside, and the concentration inside weighted by the time spent indoors. Assume that the indoor concentration for each individual is represented by the level measured inside his/her home. Figure 4 compares the mean personal levels for each individual with the mean time-weighted model estimates of exposure. Comparison with Figure 3 shows less scatter of the data about the diagonal. The r^2 has increased to 0.765, and the standard error of the estimate has decreased to 3.75 $\mu g/m^3$. The paired t for this data was 2.61, which implies the difference was still significant at the 5-percent level.

Considering the fact that such a large fraction of the time is spent indoors, it is reasonable to ask how good the indoor value by itself is as a predictor of personal exposure. Table 2 compares the correlation, paired t, and standard error of the estimate using outdoor, the time-weighted model, and indoor measurement as estimates of personal exposure. The time-weighted model does not perform significantly better than the indoor measurements alone.

TABLE 2
Comparison of Outdoor Means, Time-Weighted Exposure Model, and Indoor Means as Estimator of Personal Exposure for 37 Observations

	SULFATE			RESPIRABLE PARTICULATE		
	Outdoor	Time Model	Indoor	Outdoor	Time Model	Indoor
r^2	0.654	0.675	0.728	0.479	0.570	0.514
SEE	4.86	3.75	3.89	20.18	14.29	15.40
t	4.87	2.61	1.91	-0.85	0.71	-0.003

Respirable Particulate Relationships

Whereas the mean personal sulfate exposures are determined by outdoor sources, personal exposure to respirable particulates is determined by both outdoor and indoor sources. The Watertown personal monitoring program demonstrated the importance of smoking, as one source, in determining personal particulate exposures (12).

Comparison of the mean personal exposure with the mean simultaneous outdoor measurements (in Figure 5) shows more scatter than with the sulfates (Figure 2). In this case, $r^2 = 0.479$, and the standard error of the estimate is 20.18 $\mu g/m^3$. Again we see the clustering of the Watertown data at lower levels (outdoor mean = 17.5 $\mu g/m^3$), and the Steubenville data higher (outdoor mean = 67.3 $\mu g/m^3$). There is a tendency for higher personal values compared to outdoor values in Watertown, where smokers were included in the samples. In Steubenville, where smokers were not included, the outdoor mean values are more representative of actual personal exposure.

The paired t of -0.851 indicated no significant difference, but this apparently results from the large variance.

Personal exposure was estimated by a time-weighted combination of indoor and outdoor concentrations plus a time-weighted parameterization of smoking exposure indoors away from home. Smoking within the home is intrinsically included by the concentrations measured indoors. Smoking outside the home was estimated from the number of smokers each participant reported he was exposed to away from home. Regression analysis indicated that the impact of each smoker added 20 $\mu g/m^3$ to the average exposure. The resultant model was, therefore,

$$\overline{C} + [t_{home} \cdot c_{indoors} + t_{out} \cdot c_{out} + t_{other} \cdot (c_{indoors} + N_{smok} \cdot 20\ \mu g/m^3)] \,/\, t_{tot}$$

where $\overline{C}$ is estimated exposure to particulates, t_{home} is the time spent at home, $c_{indoors}$ is the concentration measured indoors at home, t_{out} is the time spent outdoors, c_{out} is the concentration measured outdoors, t_{other} is the time spent indoors away from home, N_{smok} is the number of smokers the participant was exposed to away from home, and t_{tot} is the total sample length.

Figure 6 compares mean personal exposures with mean values estimated by this method. The r^2 has increased slightly to 0.570, and the standard error of the estimate has decreased, to 14.3 $\mu g/m^3$. The paired t test still shows no significant difference. Personal values were regressed against just the indoor values to assess the improvement in prediction of the time-weighted model. Table 2 compares the statistics for all three methods. While using indoor values significantly improves prediction of personal values over just the outdoor values, the addition of a smoking variable gives a much better estimate. It is clear also that a best fit to the data in Figure 6 would give a non-zero intercept, indicating that there are other contributing sources and exposure factors that have not been included.

CONCLUSIONS

Although personal exposure to respirable particulates and sulfates is determined in part by outdoor levels, indoor concentrations are, because of the large fraction of time spent indoors, a much better estimator of exposure. In the case of respirable particulates, passive exposure to smokers contributes significantly to personal exposure. In addition, other activities still to be determined are adding to the particulate exposures. Further studies are planned in the relatively clean ambient environment of Topeka, Kansas, this spring in order to define these contributions.

ACKNOWLEDGEMENTS

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MAILING ADDRESS OF AUTHORS

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Discussion

(NOTE: The following discussion took place after the presentation of the papers "Design and Performance of a Reliable Personal Monitoring System for Respirable Particulates" and "Personal Exposure to Respirable Particulates and Sulfates: Measurement and Prediction.")

McCURDY: My name is Tom McCurdy. I work for the Pollutant Strategies Branch, EPA, and my comments and question are for Mr. Dockery.

Our office is doing some time averaging in high pollution exposure monitoring. We are into human activity. I also have a couple of comments. One, Chapin is not a sociologist. He is an urban planner here at the University of North Carolina. He is a physical planner. I think he would reject being called a sociologist.

Number two, there is a Dr. Robinson of Cleveland State University who has some very good time activity data. Another comment is that for modeling, we need hourly human activity data, not daily data like you aggregated. That may be true only for pollutants with a 1-hour averaging time. Have you published any of your summary of the activity data anywhere?

DOCKERY: We have presented papers at meetings in the past couple of years. It hasn't been directly published.

On the averaging time, we are doing measurements on the health effects every 3 years. And even if you get down to 24-hour average exposure, it is much finer detail than we needed in determining what our health effects are going to be, although it depends on whether the argument is the long-term average health exposure or the peak levels that are really causing the health damage.

We are trying to keep information down to the hourly level, but at least in terms of exposure, or exposure models, we are using 24-hour average values.

McCURDY: I realize that. But for our purposes, we would really like to have some hourly data. So, if you are running it, try to keep in mind the most desired aggregated time we could get for a lot of people probably is on the order of 1 hour.

One further question: I don't understand what you are saying about your regression line and your coefficient of determination.

You were putting up data that had less of an R-square value, but you were saying that you had less data in that sample. It seems to me your data were contradictory with what you were saying.

DOCKERY: When you use this correlation, you are looking at an arbitrary fit to any particular line that you can fit through there. The only difference in the one that you have compared this back to, the one-to-one reversing line, is that we are comparing his actual measurements versus some predictor, just to see how well that works.

In reality, what we are looking at is F testing, Student's t-testing, things on that order. But I didn't want to get that deep into the statistics today. I was just using the R-square as an indicator, trying to get an indicator that everybody was familiar with.

The only point I really want to make is that when we have gone to more complicated models beyond just looking at the indoor measurements, we have seen significant improvement in the statistics.

MEIER: Gene Meier, EPA. The first question I have for you is on the type of instrumentation used. Your indoor personal measurements were taken with your instrument. The outdoor numbers were obtained with what type of instrument?

DOCKERY: It is the same cyclone. And the only difference is we used a critical orifice to control flow instead of voltage control.

MEIER: The other question I had was, have you done any comparisons to ensure that you are getting the same data with the two different types of instrumentations so that that is not affecting your correlation?

TURNER: You are talking about indoor-outdoor monitoring done with both of the main orifices.

The personal exposure data were done with the commercially available monitoring unit I described.

MEIER: So, indoor-outdoor measurements were taken with the same instrument?

TURNER: Yes.

DOCKERY: I may have to qualify that a little bit, but we will talk about that later.

MEIER: The other question I have is in terms of your correlation of indoor-outdoor data. You have got a selected population group depending on your volunteers. The homes that you are looking at may not be the average home. So, even if you did find a correlation, that correlation may not hold for the population as a whole.

DOCKERY: Well, I think the jump you are making is that we can relate personal monitoring to the indoor pollution. OK; I am not saying what the relationship is between the indoor and outdoor pollution at this point. But with our more extensive indoor-outdoor network, then we can make that additional step.

MEIER: The thing that we are looking at is trying to make the correlation of the outdoor measurement to the indoor measurement--that is where we would like to go eventually.

According to your data, we cannot do that because they don't correlate well. And my question is this: whether or not in the population subgroup that you selected, you selected a very narrow group of people or homes that are either well-insulated because of their economic capability, with air conditioning, etc., the house is well-sealed, compared to what you would expect in the average population subgroup?

DOCKERY: I think that you have a legitimate point there--that we don't have a completely unbiased sample of what the population is. You know, in our indoor-outdoor monitoring, we tried to select homes based somewhat on household characteristics and on variables that we are looking to better define from this study.

As Jack Spengler said, we have gone through 2 years of this. And what we are doing now is shutting down that monitoring, going through an analysis phase, and trying to determine what the variables are that we have good handles on, and what things we don't know about. Next year we will begin a new phase of indoor-outdoor monitoring to pick up some of the other variables in the household mix.

HICKEY: John Hickey, Research Triangle Institute. You mentioned that whenever any of your volunteers went to work, the company industrial hygienists threw them out. For whatever their motives, this may have been a blessing in disguise, because the occupational limit for respirable dust is 5,000 micrograms. That may have completely masked any of your other respirable dust data, plus the fact that the occupational exposure would be a site-specific type of dust and not comparable to what they would be getting the rest of the time.

DOCKERY: That is very true. It is just a little unsatisfying to us because we have to characterize everyone in our population. We are not selecting a population because they are working or nonworking people, and especially in Steubenville, Ohio, we have a lot of steel workers, for example. We actually did get some measurements in the steel mills, but I didn't report on those.

PETERS: Edward Peters. I still don't quite understand your outdoor measurements. Did each of your individuals have a personal meter and was it directly associated with an outdoor meter?

DOCKERY: Each person has a personal meter, and each has one inside his or her home. In addition, we had our indoor-outdoor network of monitors running at the same time in the community.

So, we had five homes in each of these communities where we were taking our measurements at the same time. These were independent, in general, of the taking of the personal measurements.

It gave us a spatial distribution across the community, and that is what we were trying to define--whether there were big spatial distributions, so that if a person moved from one area of the community to another, he was getting a different outdoor exposure.

WHITE: Otto White, Brookhaven Laboratories. My question is, what is the personal exposure to the individual obtained from the personal dosimeter as opposed to a personal sample? By going to a weight-height measurement, a lot of the activities performed in the home are done at that particular height--the preparation of food, the dispensing of dry detergents.

DOCKERY: We have done some studies on this, looking at the distribution of particulates throughout the home, looking at the vertical distribution within the home. We really haven't seen any significant differences in any of the homes.

I am sure these differences exist on a short-term basis. But when you integrate that exposure over a long period of time--you know, when somebody is cooking in the kitchen, you are going to get a high peak--but when you average that out over 24 hours, the differences don't show up anymore.

WHITE: There is quite a bit of industrial data, obtained by putting duplicate samples on a worker, that show a considerable gradient exists.

DOCKERY: Clearly, it is a different case in the industrial environment. I mean, we are talking about levels that were two or three orders of magnitude lower than what you see in the industrial environment, and you know, there is rapid turnover there--air changes on the order of 1 to 2 air changes of the whole building air per hour. There is very rapid mixing within the home.

WHITE: I would probably agree with that if that sample were taken in the respirable zone--in the breathing zone.

DOCKERY: This system measures the respirable fraction of less than 3.5 microns, and you know, they have residence times on the order of days because their settling velocities are very small and they are very rapidly mixed.

I think the key to understanding the distribution is that there are multiple sources in the home--smoking, vacuuming, and everything else that can generate particulates outside the kitchen area. The monitoring we have done to look at that specific question on distribution of particulates in the home shows that it is well mixed.

Now, we are facing contradictory evidence if you look at NO_2, which Ed Palmes points out is twice as high in the kitchen area as it is in any other living area of the house. So, you have that conflicting evidence versus what we see in the fine particulates, which is well mixed; no significant differences between rooms in the house.

We also looked in the vertical, too, and we can't see any differences in the vertical.

I am not really that bothered by the difference between gases and the particulates, because when we look at the outside air pollution data, we see well-mixed particulates where you will see large gradients in the gaseous pollutants in the vertical, especially in the vertical distribution.

SHAW: Bob Shaw from EPA. Isn't is possible that if you took into account the lag between the time in which the outside levels reach a certain point and the time it takes for it to leak into the house, that your correlation might be improved? Because you could have an excellent correlation, but it may be displaced by some amount of time.

DOCKERY: Clearly, there is a buffering capacity in the home. We might see the peaks following each other. In fact, other studies have shown about a 2-hour lag in the particulates penetrating into the home.

SHAW: That would take care of it?

DOCKERY: Yes, but if that thing is happening--if we are getting a sharp peak--potentially that is getting smoothed out. Lag is something we really can't define with our sampling methods. We would have to go to the continuous monitors.

LIN: Chin-I Lin, Lawrence Berkeley Laboratory. I would like to know more about the measurements associated with the study, since one of your slides showed indoor-outdoor pollution correlated better in wintertime than in summertime. I would have expected it to have been the other way around. Do you have any comment on that?

DOCKERY: I have looked at these data by season, and they showed much better correlation in summer than winter. These indoor-outdoor data that we presented are, you know, gross means. I don't think they are a good representation of what the real situation is.

When you look at individuals, however, the correlation is much, much higher in the summer than in the winter.

LIN: Do you make ventilation rate measurements in these study homes?

DOCKERY: We don't have a good indicator of ventilation. That is also in the planning stage; we are trying to include it in our next series of measurements. That is a real key.

WALLACE: Lance Wallace, EPA. Have you looked at the levels in traffic as compared to indoors or outdoors? At least, I have noticed in my CO data, for example, that I have got more CO in the 2 hours I commuted than in the other 22 hours per day.

DOCKERY: Let me comment on that. I philosophically don't believe it is important, because when you look at the amount of time you are spending in traffic, we are showing, and other studies have shown, that an hour per day does not have a really significant impact, unless you are going to have 8 times or 20 times as much exposure in traffic.

We have got some data that show considerably higher particulate levels in traffic. But I don't think they are large enough to really be of significant impact.

I think that the key right now is the ventilation rate, as Dr. Lin mentioned--trying to determine that and relate that back to the data. We can get information on the sources within the home, but if we don't know the ventilation rate of the home, then we aren't able to parameterize that out.

SPENGLER: I feel like you do. This is where we have our difference. We have done a lot of condensation nuclei counts in traffic. The highest counts I ever see are associated with roadways and in automobiles. The order is a magnitude higher. I think that is one exposure category with associated exposure patterns that we have to define more carefully.

WALLACE: One might expect that the dust in traffic, particularly the lead, and the gases have to be more toxic than the pollution in the home.

The Tandem Filter Package

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INTRODUCTION

The use of chemically treated filters to absorb gases of interest from an air stream passing through the filter is not new. A computer-assisted search of the literature has turned up about 20 research papers in which recipes for filter treatment are reported--the oldest of which was published in 1954. References are given here only to those papers appearing in the published literature (1-14).

Almost all of this reported work is concerned with SO_2 and/or H_2S. The recipes for SO_2 collection include carbonates or bicarbonates (seven papers), hydroxides (six papers), and zinc acetate, ferrous sulfate, tetrachloromercurate, and hydrogen peroxide (one paper each). The recipes for H_2S collection include lead acetate (four papers), silver metal membrane (one paper), and silver nitrate (three papers). Only a few of these papers report the use of a prefilter for aerosol particles.

In addition to the work cited above, atmospheric analysis using chemically treated filters is reported by the British Factory Inspectorate for 26 dangerous gases, fumes, and dust in a particularly interesting series of booklets (22). These methods are intended to detect levels higher than the threshold limit values.

The initial motives of the EPA's Inorganic Pollutant Analysis Branch (IAPB) in developing the tandem filter package were: 1) to provide a means of

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separating and collecting various particulate and gaseous components of the atmosphere; 2) to provide separation of the various chemical species of sulfur in gaseous compounds (e.g., SO_2, H_2S, etc.); 3) to permit the sample collection analysis to be carried out as simply and cheaply as possible with a minimum of operator intervention but with sufficient sensitivity to allow measurements at low (e.g., rural) levels; and, 4) to collect these components in a manner suitable for elemental analysis using our X-ray fluorescence (XRF) spectrometer.

The tandem filter package (TFP) consists of a series of filters in tandem, each of which collects a different component from the air stream passing through it. Aerosol particles are collected on porous, nonreactive filters through which gases will pass (ideally) without effect. Gases are collected on filters which are individually treated with reagents which will absorb and fix the gas of interest. The following sections describe the TFP which we have developed. It separates and collects coarse and fine aerosol particles, SO_2 and H_2S. Analysis for elements present in the collected aerosols is carried out by X-ray fluorescence. Analysis for sulfur is by X-ray fluorescence or by wet chemical extraction of the collection filters; and analysis of the extract is by the Thorin-Brosset colorimetric procedure, by ion chromatography, or by flash pyrolysis into a flame photometric detector. Development and evaluation of the system for other atmospheric gases (e.g., NH_3, nitrogen oxides) are continuing.

AEROSOL COLLECTION

The choice of filters for collection of aerosol particles is based on results by workers in the IPAB and their collaborators (15), and others (16). Briefly, one uses a front filter of large-diameter pores which collects larger particles, and a second filter of smaller-diameter pores to collect small particles. We currently use a Nuclepore filter with 8- or 12-μm diameter pores, and either a Nuclepore filter with 0.4-μm diameter pores or a Fluorepore (Teflon) filter with 1-μm diameter pores.

The collection efficiency of Nuclepore filters of large-pore diameter has been studied in great detail by Parker (17), and that for small-pore diameter filters by Liu and Kuhlmy (16). Their results show that collection efficiency depends on many factors: velocity of the air stream through the filter, particle density, filter porosity, filter flow resistance, etc. Roughly speaking, however, the large-pore diameter filter collects particles larger than 3-μm diameter, and the small filter collects particles at least down to 0.03-μm diameter with nearly 100 percent efficiency. The minimum in the well-known bimodal mass distribution for typical atmospheric aerosols occurs for particles having diameters around 3 μm; and the deposition of particles during breathing occurs such that, very roughly speaking, particles larger than 3 μm do not reach the lower areas of the human respiratory system.

Recent work by John et al. has shown that the tandem filters separate solid and liquid particles with significantly different efficiencies (23). These results, and our own experience (26), indicate that tandem filters give only an approximate separation of fine and coarse particles.

CAPACITY OF THE PUMPING SYSTEM

In choosing a pumping system for the TFP, one is faced with the usual compromise between the desire for the highest possible sensitivity and the requirements that the system be relatively portable, compact, inexpensive, etc. The specific requirements placed on the pumping system for rate of flow through the filter depend on: 1) the atmospheric abundances of the elements of interest, 2) the time permitted for sampling, and 3) the sensitivity of subsequent analysis.

To illustrate how the above conditions dictate our choice of pumping systems, let us say that we desire to be able to detect the gases SO_2 and H_2S at the 1 ppb (V/V) level and that the sampling time should be no longer than 8 hours. Our X-ray fluorescence analysis system has a sensitivity to S such that about 1 μg can be detected quantitatively (to 10 percent). At 25° C and 1 atmos, the concentration of S in H_2S or SO_2 at 1 ppb is 1.3 $\mu g/m^3$. Hence, to accumulate 1 μg of S on a filter of 100 percent efficiency, we must pass about 3/4 m^3 through it, and, to achieve this in 8 hours, the pump must have a rate of about 1.6 l/min.

A pump, which will have the necessary capacity determined by considerations as outlined above, must be able to sustain the pressure drop which occurs across the filters at the desired rate of flow. Liu and Kuhlmey (16) have measured coarse and fine particle collection efficiencies as a function of pressure drop for various commercially available filters. The pressure drop across the 1 μm Fluorepore filters used in this work for both fine particle and gas collection is 10 Torr at a face velocity of 13 cm/sec. For an exposed filter area of 8 cm^2, this face velocity corresponds to a flow rate of about 6 l/min. For lower flow rates the pressure drop is correspondingly lower, but Liu and Kuhlmey do not present any data for pressure rops less than 10 Torr. We conclude that for a filter pack consisting of 3 1 μm Fluorepore filters, the pump must be capable of sustaining a pressure drop of 30 Torr if the flow rate is to be 6 l/min. For lower flow rates the pumping capacity is lower, and, hence, the requirements on the pumping system are rather modest.

The pressure drop results quoted above are due to the resistance of the filters to flow. As particles are collected on the aerosol filters, this "loading" will increase filter resistance and, for very heavy loadings, affect the sampling rate. For Teflon filters, the impedance doubles at a loading somewhat less than 100 $\mu g/cm^2$ (18). Recent analyses of air samples in major U.S. cities gave total suspended particulates in the 20 to 60 $\mu g/m^3$ range (19). We conclude that filter loading is unlikely to cause excessive demands on the pumping system for the TFP.

Size and weight limitations for a personal dosimeter create a severe limitation on suitable pumps. A survey of personal sampling pumps by Parker et al. (24) shows that none of a range of commercially available personal sampling pumps can support the TFP given the demands outlined above. We have used the Brailsford pump with the TFP in the field with good results, and a compact and portable personal monitor using this pump has been developed by Turner et al. (24).

GAS SAMPLING--SULFUR COMPOUNDS

The treated filter development for separation and collection of SO_2 and H_2S is based largely on the work by Huygen (13,14), who found that the rate of uptake of these gases in the filter media was increased with increased humidity. Huygen explained this behavior by attributing the rate of uptake to diffusion into the liquid phase created by condensed moisture on the filter. We add triethanolamine (TEA) to our collection solutions to provide a hygroscopic material which will keep the filter surface wet.

Sulfur is a relatively light element, and its X-rays are, correspondingly, of relatively low energy. Consequently, if the sulfur is collected in the bulk of the filter rather than on the surface, severe attenuation of the emitted X-ray intensity will occur during X-ray fluorescence analysis. In order to collect the sulfur gases on the surface of the filter, the collection solution is applied to the filter surface in an aerosol spray. The filter medium used is Teflon (Fluorepore), and, in order to prevent the aqueous solution from accumulating on the hydrophobic Teflon surface in large drops, sufficient isopropanol is added to the solution to permit the solution to wet the filter surface.

The absorbing and fixing agents for SO_2 and H_2S are NaOH and $Cu(NO_3)_2$, respectively. The absorption of SO_2 into basic solutions is well known. In a basic environment, the sulfurous acid equilibrium is strongly shifted to the ionized state, and the escape of SO_2 is hindered. Eventually, the bisulfite or sulfite ion presumably undergoes further oxidation, possibly by atmospheric oxygen, to $SO_4^=$, and is fixed in the filter solution. The reaction of H_2S with metals and metal salts in the presence of water is also well known. The reaction causes the formation of unsoluble, often colored sulfides, which serves to fix the sulfur. Other workers have used Ag or Pb for this purpose; however, these elements have X-ray transitions which can interfere with detection of the S X-ray and, hence, are not suitable for X-ray emission analysis on our instrument. We have chosen a salt of Cu which is tarnished by hydrogen sulfide and which has no interfering X-ray transitions. The H_2S collection solution does not collect $(CH_3)_2S$.

The solution recipes for the SO_2 and H_2S collection filters are:

	2M NaOH(aq)	0.1 M $Cu(NO_3)_2$ (aq)*	TEA	Isopropanol
SO_2	55%	--	27%	18%
H_2S	--	45%	18%	37%

*The H_2S solution is acidified to 0.01M with HNO_3

These recipes have not been systematically optimized, and adjustments in relative amounts of their components may improve their collection properties. Work is continuing on the evaluation of the chemically treated filters under varying conditions; e.g., gas concentration and humidity.

CHEMICAL ANALYSIS OF FILTERS

Analysis for sulfur as $SO_4^=$ can be carried out using ion exchange chromatography, or the Brosset-Thorin method (25). Filters are extracted by placing them in a polypropylene bottle along with 10 to 20 ml of 5×10^{-5}N perchloric acid. The bottle is put in a sonic bath for 20 minutes.

Spectrophotometric-Thorin

The spectrophotometric-Thorin method was first presented by Persson (21) and later modified by Brosset et al. (22). With two exceptions, this method is identical to that proposed by Brosset et al.; instead of using Dioxane or acetone as a solvent, isopropanol is used, and sulfanazo is used to obtain a reference intensity level. Before analysis with the spectrophotometer, the extracted solutions are put through an ion exchange column using Dowex 50W-X8 50-to-100-mesh ion exchange resin. The columns are 15 cm long. The spectrophotometer used is an Hitachi Model 101. Calibration is accomplished using a primary solution of 0.1N H_2SO_4 (Fisher) and diluting to cover the range 10^{-4}N to 10^{-5}N in five steps. Five readings are taken at each concentration, and the data are fit to a linear function by the method of least squares. The calibration is done once for each set of samples or at least once each day. Quality control solutions are run for each calibration curve. Analysis of data shows the minimum detectable level for this method to be 5 neq/ml. Concentrations can be determined to within ± 5 percent.

Ion Exchange Chromatography

The second method used to determine sulfate is ion exchange chromatography. The chromatograph used is a Dionex Model 14. If the sample has been extracted using an acid, it is spiked with a base (.003M $NaHCO_3$ + 0.02 M Na_2CO_3) before running on the chromatograph. Calibration is accomplished by mixing sodium salts (Fisher) with a buffer. Retention times and peak areas are obtained from these standards, and a calibration curve is drawn. Analysis of sulfate data shows the minimum detectable level to be 10^{-1} neq/ml. Concentrations can be determined to within ± 10 percent.

Several SO_2 collection filters have been analyzed using the above procedure. Table 1 shows the results for sulfur determination for three SO_2 collection filters by X-ray fluorescence analysis (XRF) and subsequently by extraction of the filter and ion exchange chromatography (IC).

TABLE 1

Comparison of XRF and IC for Sulfur Analysis

	Sulfur (μg)	
Filters	XRF	IC
715407	3.1	3.2
715408	3.9	3.7
715411	2.9	2.8

Chemical analysis of S on the H_2S filters can be carried out using ion exchange chromatography, but the $S^{=}$ must be converted to $SO_4^{=}$. We are currently investigating conversion procedures--in an initial experiment, we used a solution of H_2O_2 for extraction and conversion, and observed a peak corresponding to $SO_4^{=}$ of about the expected size on the chromatograph. A major interference occurs, however, because NO_3^- from the H_2S collection solution elutes from the column just before the appearance of $SO_4^{=}$, and the tail from the NO_3^- peak interferes with the quantitative determinations of $SO_4^{=}$. This interference could be avoided by using a different acid and copper salt (e.g., Cu acetate and acetic acid) in the collection solution.

Flash Pyrolysis with Flame Photometric Detector

A third wet chemical analysis for S is by sudden (flash) pyrolysis of the extraction solution on a heated metal strip, and detection of S in a flame photometric detector. Initial experiments using the extraction solutions from H_2S filters indicated the feasibility of this technique, but it has not been developed further.

Summary of Chemical Analysis of Filters

Sensitivities of these various analyses for S are shown in the following table, which assumes extraction of the filters into 10 ml of solution. The following amounts can be determined to ± 20 percent or better:

Brosset-Thorin	800 ng
ion chromatography	16 ng
pyrolysis-FPD	320 ng

THE TFP HOLDER

We have designed a filter holder that is based on two principal criteria: 1) maximum simplicity and 2) minimum expense. An exploded view of the TFP is shown in Figure 1. The filter frames are aligned by the four bolts which hold the assembly together. The functions of the "O" rings as shown in Figure 1 are to hold the filter in the frame and to provide a pressure seal to the next filter in line or to the holder assembly. It is sufficient to turn the screws down finger tight to provide an adequate seal. In Figure 2 we show a schematic drawing of a tandem filter package mounted on a pump assembly. In this arrangement, the flow rate is controlled by a critical (limiting) orifice. Although these orifices provide flow control in a very simple way,

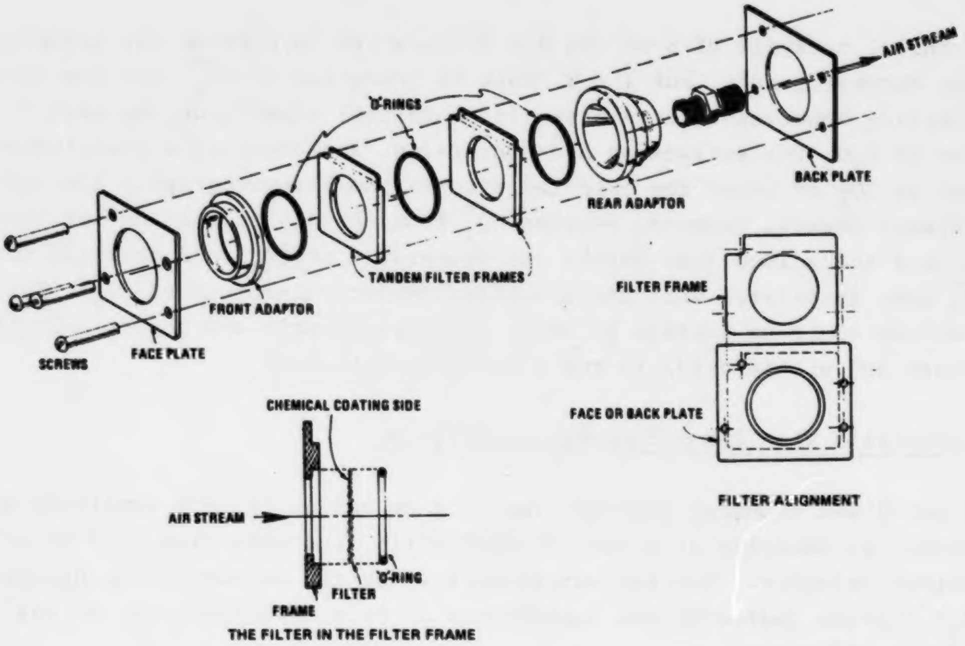
AIR STREAM
'O' RINGS
BACK PLATE
REAR ADAPTOR
TANDEM FILTER FRAMES
FRONT ADAPTOR
SCREWS
FACE PLATE
FILTER FRAME
FACE OR BACK PLATE
FILTER ALIGNMENT
CHEMICAL COATING SIDE
AIR STREAM
'O' RING
FILTER
FRAME
THE FILTER IN THE FILTER FRAME

FIGURE 1. Tandem Filter Pack, exploded view.

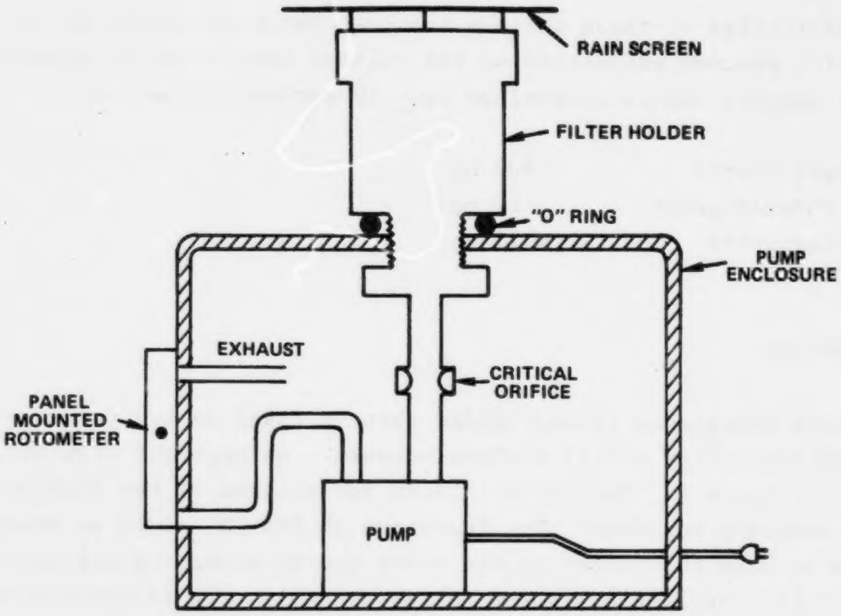
RAIN SCREEN
FILTER HOLDER
"O" RING
PUMP ENCLOSURE
EXHAUST
CRITICAL ORIFICE
PANEL MOUNTED ROTOMETER
PUMP

FIGURE 2. Tandem Filter Pack and pumping system.

they have the disadvantage of requiring applied vacua of 300 and 550 Torr for 1.0 liter/minute (l/min) and 14 l/min orifices, respectively. A simple alternative to the critical orifice is a calibrated rotameter (flow meter) with a limiting needle valve. Our experiments indicate that the filter frame-filter "O" ring assemblies will not tolerate flow rates greater than 2 l/min (filter face velocity of 250 cm/min). At higher flow rates, the filters pull away from the frames. This can be avoided by using an adhesive to seal the filters to the frames. We are now investigating the use of Teflon filters bonded to the frames.

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Discussion

TRAYNOR: Gregory Traynor, Lawrence Berkeley Laboratory. You said that not having a fine cut point may be a disadvantage in the tandem filter. Wouldn't it be an advantage since your nose and lungs don't have a fine cut point?

SHAW: Well, you could take that point of view. And in fact there was a big discussion recently at EPA having to do with the question of what sort of samplers should be used in order to determine inspired-respired particulates in the atmosphere.

I guess that my understanding of the discussion is that because people's lung capacities are so different, and because it makes a difference whether you are mouth-breathing or nose-breathing, and your level of ventilation, that the inspiration curves are quite different between individuals. It may be better to settle on some precise separation scheme rather than trying to limit the human lung.

TRAYNOR: There is something that we do know. We know that the human lung is not precise.

SHAW: Yes. Well, I can't say any more than I did. There is no average human lung, so to speak. If there were, then you would want to repeat the behavior--no doubt about it. But since different lungs act so differently, the decision has been made to separate the particles according to their two modes. There is more information on that.

GUDAP: Bill Gudap, Research Triangle Institute. Bob, do the essentially damp or wet filters cause any problems?

SHAW: No, because the layer is very thin. So, they go right through the X-ray spectrometer with no trouble. Actually, water doesn't adsorb X-rays very strongly. And so that thin layer doesn't cause any trouble.

BROOKS: Joe Brooks, Monsanto Research Corporation. I have a question concerning the pumps. Do you know what kind of pressure drops these pumps will tolerate?

SHAW: Yes. The Brailsford can support 50 mm of Hg, pressure drop at about 4 liters a minute. We use it to pump across some sampling devices which have a much bigger pressure drop than this. This device has a very small pressure drop. I don't know what it is, but it is much less than 50.

WHITE: Otto White, Brookhaven Laboratories. I am not sure that I understand the comment about the comparison between the radiation exposure where you wouldn't see the data for several days. I think my colleagues might be at odds with me if I didn't comment, but there are pocket dosimeter devices which can alarm. I think in this particular area--at least in the industrial area--that you have similar type instrumentation where you want some type of alarming device--such as the CO monitor talked about in a paper presented earlier.

And you may have an accumulative device. So, I am not sure that I understand your meaning.

SHAW: Yes; I remember from the old days that when I would walk out of the room where the scattering chamber was, I would occasionally wonder how much exposure I had gotten while I was in there. We didn't have the kind of dosimeters that you are talking about.

I was just trying to make a point that this particular system requires that it be sent back to the lab for analysis.

One could develop chemically treated filters that would respond colorimetrically so that you could compare right on the spot with a prepared scale. But the system that we have now doesn't do that.

WHITE: I think both types of systems are appropriate. And whether or not you want that type of immediate response depends upon the need for a gross estimate.

ZISKIND: Richard Ziskind, Science Applications. You are going to get sulfate dioxide converted to sulfate. You are also going to get sulfate from the air. You can't discriminate between those, can you, with the dosimeter?

SHAW: If you remember, the first couple of filters took out the particles and let the gases go through. And the next filters down the line took out the gases according to their chemistry. So, that is how you get the separation.

An Evaluation of Personal Sampling Pumps in Sub-Zero Temperatures

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INTRODUCTION

The development of the large oil reserves along the northern slope of Alaska's Brooks Range and nearby Prudhoe Bay typifies the industrialization currently taking place in cold environs. These developments--precipitated by America's growing dependency on foreign oil, with its inherent threat of crippling embargoes--are taking place in a severe environment which tests the endurance of both men and machines. The growth of industrialization in these and other cold regions has generated a growing need for air sampling instrumentation and methodology suitable for industrial hygiene investigations in sub-zero temperatures. With a view toward these needs, the authors have investigated the suitability of currently available personal sampling pumps for use in cold environs; i.e., to temperatures as low as -50° C. This paper is a brief presentation of the results of these investigations. A detailed description of these investigations is available in the Project Final Report (1).

The pumps evaluated were tested at temperatures between 25° and -50° C. While many environmental factors or stresses act in synergism with temperature, most are of significance only at high temperatures and were not incorporated into this experimental program. An environmental factor which does have an important synergistic relationship with temperature at low temperatures is humidity. Absolute humidity is low in cold environs; thus, air sampled during these tests was obtained from a dry air manifold.

The personal sampling pumps evaluated can be categorized into two different groups. One group is the Coal Mine Dust Personal Sampling Units (CMDPSU), for which a certification program has been defined (2). In order to be certified, the CMDPSU pumps must be capable of operating from their internal battery packs at a nominal flow of 2 liters-per-minute against a resistance of 4 inches of water for not less than 8 hours, presumably at room temperature. (There are other requirements.) This performance requirement was used as a test condition for the evaluation tests described herein.

The second class of pumps is used with a variety of sample collection devices under a variety of conditions. This suggests--and it is true--that these pumps, in the aggregate, provide industrial hygienists a wide range of sampling capability. A given pump, in contrast, may only function over a narrow region of the aggregate range. Thus, it is impractical to define a single set of test conditions which will be meaningful in terms of the capability of all of these pumps. The practice adopted for these evaluations was to test each pump under a set of conditions which was somewhat representative of each pump's capabilities as stated by the manufacturer. Consequently, the data reported herein are not intended to be used to compare one pump against another. Instead, these data are intended only to demonstrate how each pump's operation is affected by a low-temperature environment.

THE ALASKAN ENVIRONMENT

Since it was the rapid industrialization of the Alaskan oil fields that largely precipitated these studies, it is of interest to briefly characterize the Alaskan environment. North and central Alaska are divided into two climatic divisions by a 600-mile stretch of low but rugged mountains known as the Brooks Range. This expanse of mountains forms a natural partition between the Interior Basin to the south and the Arctic area to the north. The Alaskan oil fields are located along the harsh, sub-zero environs of the north slope of the Brooks Range; this is an area of primary concern.

The north slope of the Brooks Range is located in one of four extremely cold winter regions. (The others are Greenland, northeast Siberia, and the Antarctic.) In this region, the average temperature in January is -24° C, and in July is 8° C. The temperature in some areas is below -40° C at least 10 percent of the time in the coldest month. The diurnal cycles are very weak, and very low temperatures can persist for several days. At Pt. Barrow in the Arctic area, for example, temperatures below -34° C have persisted for as long as 12 days, and temperatures below -40° C have persisted for 2 days. Temperatures of approximately 24° C have been observed at Pt. Barrow in midsummer, but the average midsummer temperature at Pt. Barrow is only 2° C.

While extremely low temperatures largely characterize the Alaskan environment, there are other features which may also affect the responses of personal sampling pumps. The absolute humidity, for example, is very low in extremely cold environs. (The relative humidity is usually very high.) The average precipitation is low, but it is usually in the form of solid precipitates.

TEST PROTOCOL

Most of the low-temperature tests described were conducted in a test chamber which was cooled with liquid nitrogen. Figure 1 is a schematic of the basic test facility. A pump under test sampled air metered from a dry air manifold. The sample air passed through a heat exchanger inside the test chamber so that it was also cooled to the test temperature. The pressure drop across the pump was measured with a water manometer located outside the test chamber. The sample air was exhausted inside the chamber at the test temperature. As illustrated, provisions were made in each pump to substitute a power supply for the pump's batteries when the batteries became a performance-limiting factor. The volumetric change in the air mass between the rotometer (at room temperature) and the pump (at test temperature) is accounted for in the data presented herein. Corrections for pressure variations were small and are neglected.

TEST RESULTS

In the following paragraphs, some typical test results are presented for the pumps that performed best. The reader is cautioned that there is some variance between pumps of a given model and some day-to-day variance for a single pump. These data are presented as being somewhat typical although they are from a single unit of each pump. As many as five units of each pump were tested.

Mine Safety Appliances Company (MSA), Model G

The Model G is a certified CMDPSU pump and was tested with CMDPSU requirements in mind. Figure 2 is a data plot that illustrates the flow rate

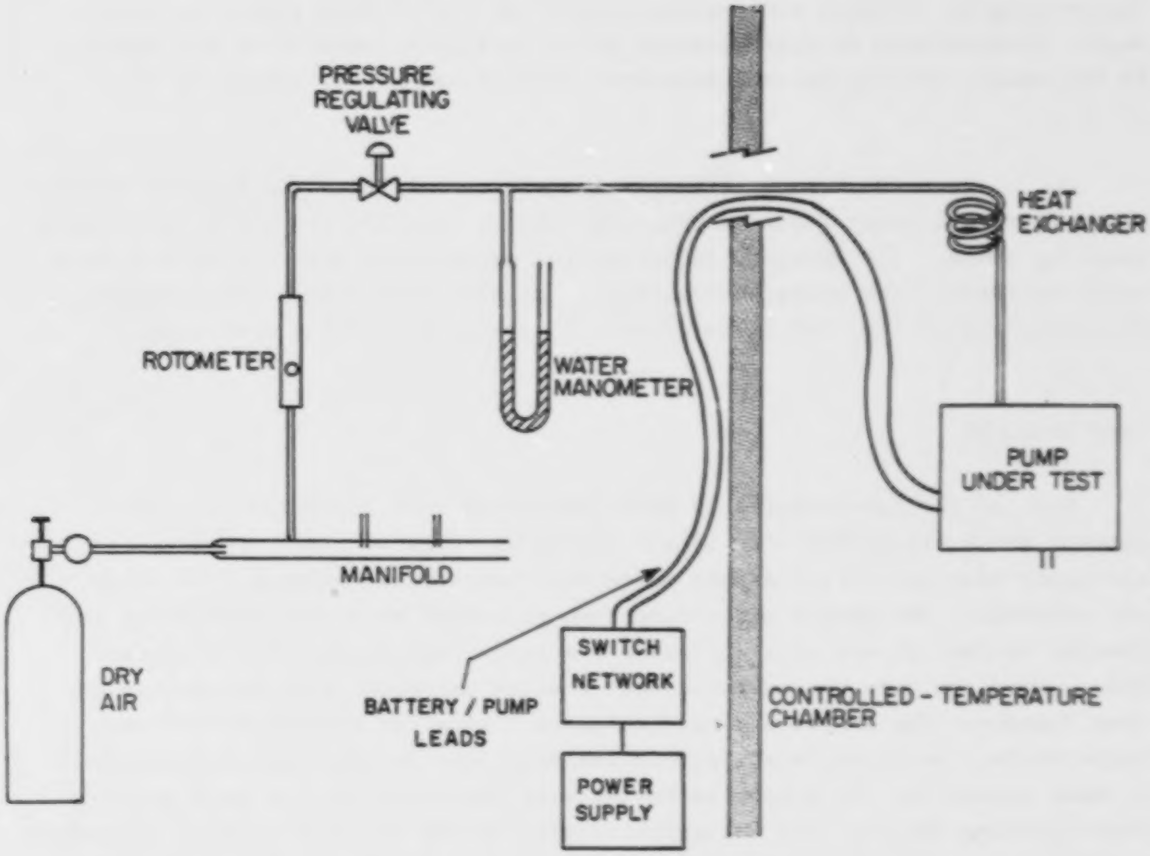
PRESSURE
REGULATING
VALVE
HEAT
EXCHANGER
ROTOMETER
WATER
MANOMETER
PUMP
UNDER TEST
MANIFOLD
SWITCH
NETWORK
DRY
AIR
BATTERY / PUMP
LEADS
CONTROLLED - TEMPERATURE
CHAMBER
POWER
SUPPLY

FIGURE 1. Schematic of the basic test facility.

stability of the Model G over an 8-hour period. The pump "load" or pressure drop was approximately a constant and was 4 inches of water. During these tests, the flow rate was sometimes adjusted to a maximum, and a power supply was sometimes substituted for the pump's battery pack. These events are clearly marked in Figure 2 and in other data plots which follow.

The data in Figure 2 show a marked flow rate dependency on temperature. They show a significant pumping capability at -11° C and even at -22° C without any adjustments. All were marginal at -30° C, and none were even marginally satisfactory at temperatures below -30° C.

In Figure 3, flow rate is shown as a function of pressure differential across the pump with temperature as a parameter for a different Model G. These data were acquired after the pump equilibrated, nonoperating, at the test temperature for 1.5 hours.

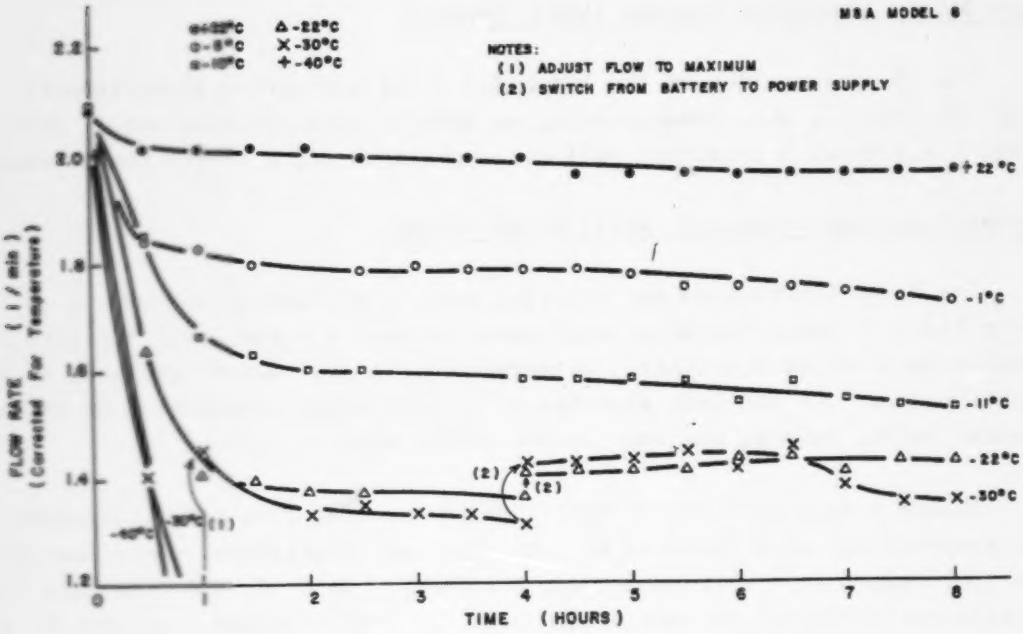

FIGURE 2. Flow rate stability, corrected for temperature, Model G.

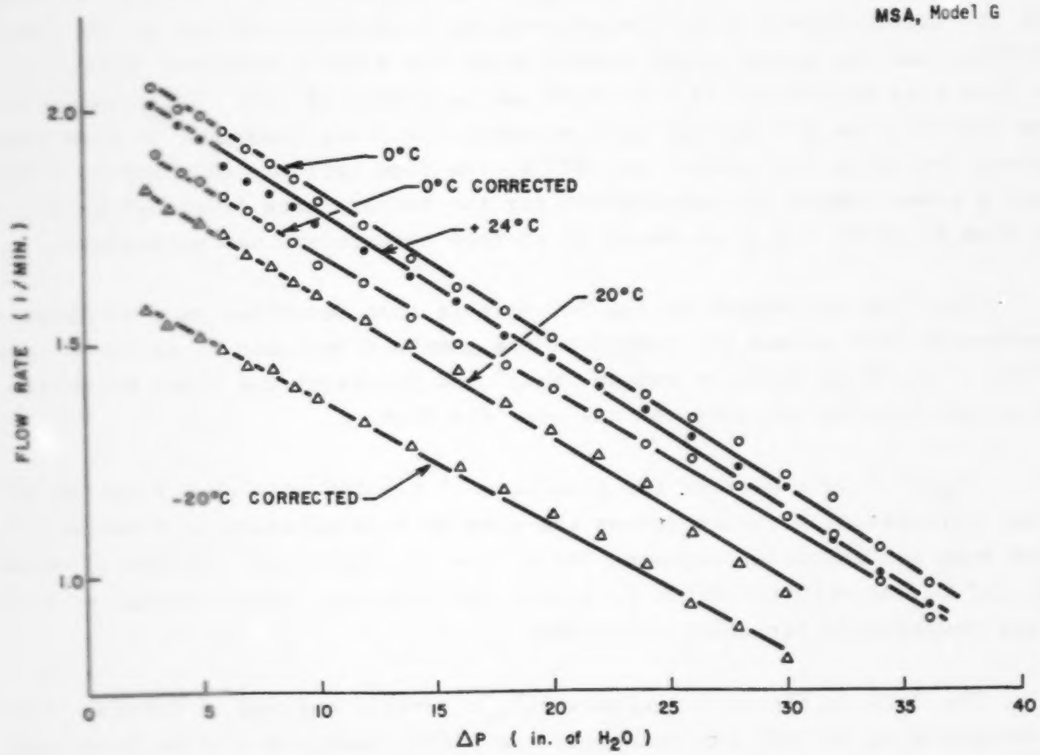

FIGURE 3. Flow rate versus pressure differential, Model G.

Mine Safety Appliances Company (MSA), Model S

The characteristics of the MSA Model S did not differ significantly from the Model G, and, consequently, no Model S data are presented. Both the Model G and Model S performed well as compared to other CMDPSU pumps tested.

Research Appliance Company (RAC), Model 2392PS

The Model 2392PS personal sampling pump is configured for use as a 2 l/min pump; i.e., it has a rotometer calibrated between 1.6 and 2.0 l/min with a resolution of about 0.1 l/min. Consequently, it was tested similarly to the CMDPSU units. The RAC unit also has a similar series arrangement of rotometer, control valve, damper, and pump as the CMDPSU units.

Figure 4 is a plot of the Model 2392PS measured flow rate, corrected for the temperature, as a function of both time and temperature. As illustrated, the room temperature performance was excellent. At 0° C, the flow rate was significantly reduced but was stable over the 8-hour period. At -10° C, its performance was marginal, and both a flow rate adjustment and a power supply substitution were made in an attempt to maintain a satisfactory flow rate. At low temperatures, flow rate adjustments have little effect on the Model 2392PS, and the power supply substitution was also of marginal value. At -20° C, a flow rate adjustment at 1.5 hours had no effect at all. The pump continued to operate from its battery pack at about 1.4 l/min (measured at room temperature) for about 5.5 hours. At -30° C, the flow rate was adjusted to a maximum, and a power supply was substituted for the battery pack after 1.5 hours; thus, a flow of about 1.2 l/min measured at room temperature was maintained.

The flow adjustment on the RAC unit is best described as a pinch or clamp mechanism that clamps and restricts the sample flow tubing. At low temperatures the tubing tends to remain "set," and releasing the clamp mechanism does not provide positive control over the flow.

Figure 5 is a plot of the flow rate of the RAC unit as a function of the differential pressure across the pump with temperature as a parameter. The pump was initially adjusted for a flow of 2 l/min at 4 inches of water at 21° C. As with the Model G, it was equilibrated, nonoperating, at each test temperature for about 1.5 hours.

The data in Figure 5 includes 21°, 0°, -10°, and -20° C curves. Curves corresponding to both the measured flow rates (measured at room temperature) and curves corrected to correspond to the test temperatures are included.

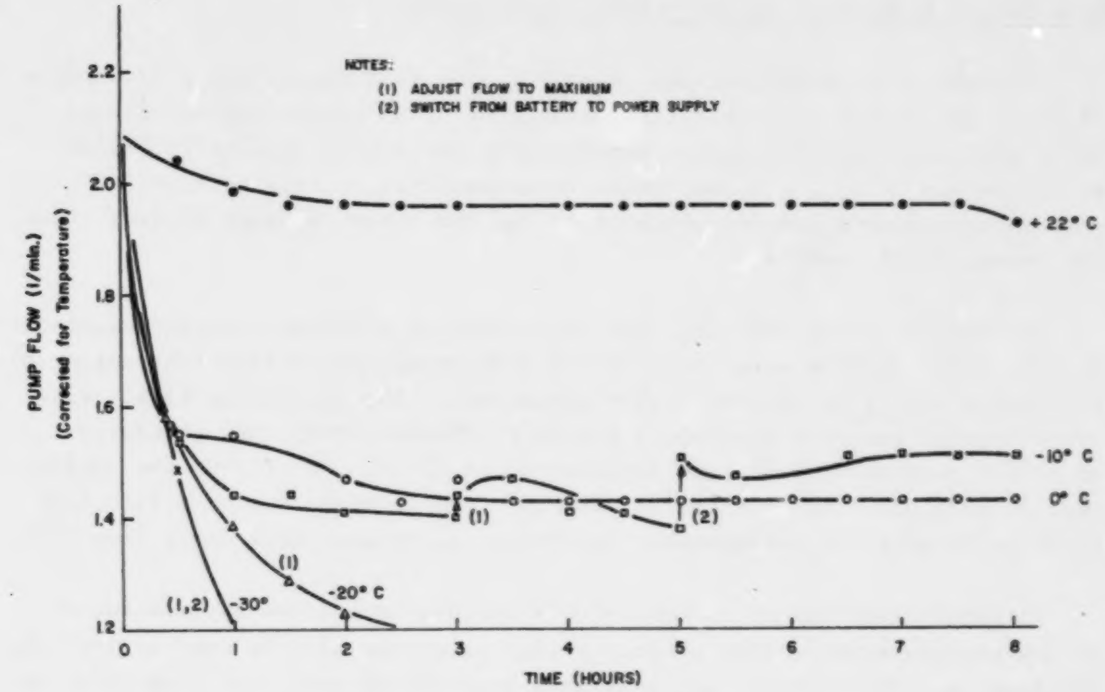

FIGURE 4. Flow rate stability, corrected for temperature, RAC Model 2392PS.

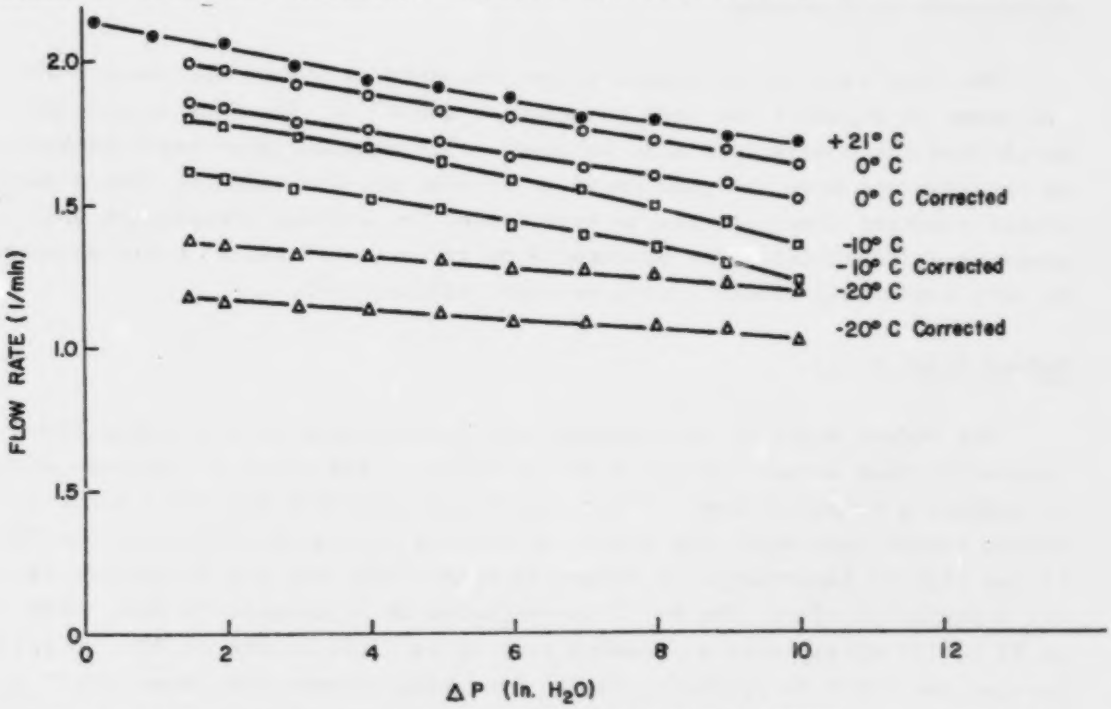

FIGURE 5. Flow rate pressure differential, RAC Model 2392PS.

Mine Safety Appliances Company (MSA), Model C-200

The MSA Model C-200 personal sampling pump is designed for a flow range of 25 to 200 ml/min through a flow resistance of up to 2.5 inches of H_2O. It is nominally adjusted by the manufacturer for a flow rate of 200 ml/min at 1.5 inches of H_2O, and most tests were conducted at this setting. The pump incorporates a counter which indicates the number of pump strokes--thus, the volume of air pumped.

Without altering the flow rate adjustment as received from the manufacturer, the Model C-200's were operated for 8 hours against a flow restriction of 1.5 inches of H_2O at several test temperatures. The results of these tests for a typical pump are plotted in Figure 6. These curves show generally excellent performances at room temperature at -2° C. At -10° C, the performance is marginal. In other units, the 10° C performance was unsatisfactory. In no units were the performances acceptable at temperatures lower than -10° C.

A significant factor in the C-200's failure to perform satisfactorily at low temperatures is that a mercury (Hg) reference cell is used in the pump's electronics. Two voltages are available from the Hg cell, and these were observed to decrease significantly with a decrease in temperature to limit low-temperature performances.

The flow rate versus pressure-drop characteristics of the Model C-200 are shown in Figure 7 for room temperature and 0° C. The flow rates computed from the counter are also included. The constant flow rates indicated by the counters show the pump speed to be constant and indicate that a very stable constant flow rate can be anticipated for a given temperature and pressure differential. The measured flow rates at 25° and 0° C are observed to vary reasonably linearly with pressure differential.

DuPont Model P-125

The DuPont Model P-125 sampling pump incorporates an electronic flow controller that senses the air flow and controls the speed of the pump motor to achieve a constant flow. Other distinctive features include a battery charge status indicator, and a flow monitoring indicator that trips and latches if the flow is interrupted or cannot be maintained near the calibrated value for a period of time. The P-125 is specified as adjustable to flow rates of 25 to 125 ml/min with a pressure drop of up to 25 inches of H_2O. Significantly, the P-125 is specified for an operating temperature range of -7° to 49° C.

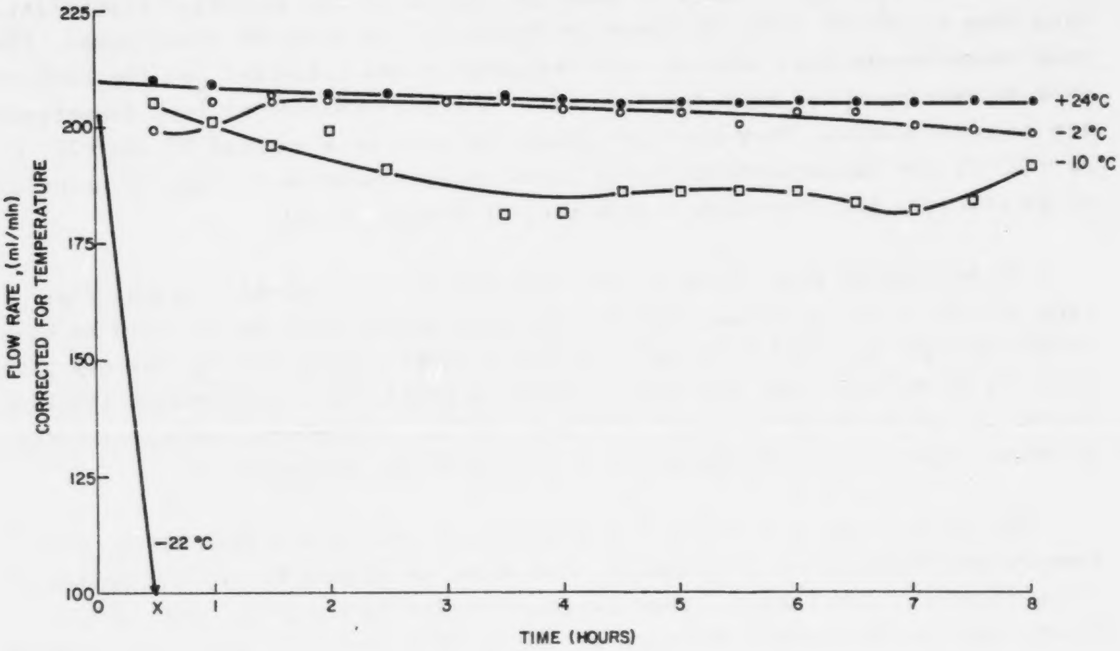

FIGURE 6. Flow rate stability, corrected for temperature, Model C-200.

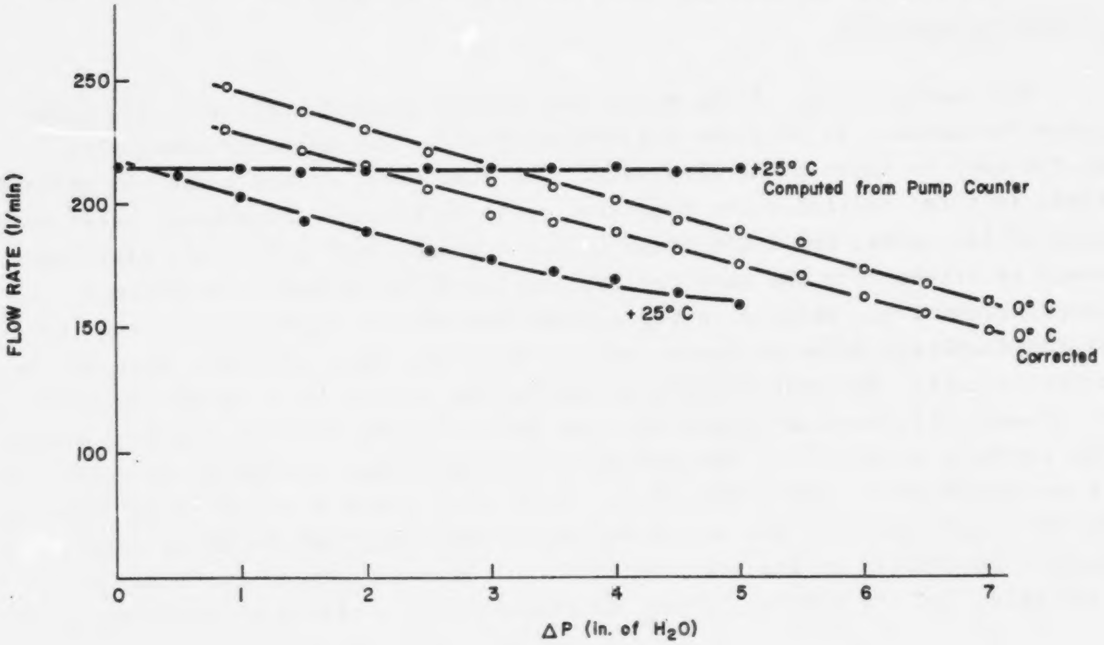

FIGURE 7. Flow rate versus differential pressure, Model C-200.

The flow rate stability of the P-125's was measured at 100 ml/min and 10 inches of H_2O; i.e., somewhat near the middle of the specified capability. Data from a typical unit are shown in Figure 8. As with the other pumps, flow rate measurements were made at room temperature and corrected for the difference between room and test temperatures. The performances at room temperature are notably stable. They are also generally good at a nominal 0° and -22° C. At -22° C, the temperature-corrected flow rates tended to be high by about 15 to 25 percent, but they were stable over an 8-hour period.

It is notable that three of the five P-125's maintained a useful flow rate at -30° C for an 8-hour period, and that useful flow rates could be maintained at -30° and -40° C by substituting a power supply for the battery pack. Thus, it is evident that the battery pack is a principal performance-limiting factor in the DuPont P-125 at -30° C and -40° C. Therefore, useful sampling at these temperatures may be possible with a larger battery pack.

The flow rates of a P-125 as a function of pressure differential, with temperature included as a parameter, are shown in Figure 9. In the aggregate, these data show remarkably linear characteristics between +25° and -20° C. These results are further evidence of the P-125's generally excellent performance at temperatures as low as -20° C.

Accuhaler Model 808

The configuration of the Model 808 differs significantly from the other pumps evaluated. It utilizes a limiting orifice that attaches integrally to the pump to control the flow rate. The pump motor drives a pin-cam mechanism that, in turn, initiates the following cycle of events. An exhaust valve to a pump cavity opens, and a diaphragm (i.e., a piston with a flexible diaphragm seal) is driven into the pump cavity, causing it to exhaust. At maximum compression--i.e., minimum cavity volume--the exhaust valve closes, and the piston/diaphragm drive mechanism springs back to a null position, opening the motor circuit. The piston/diaphragm mechanism, driven by a spring, returns to an extended, maximum-volume position as air bleeds into the cavity through the limiting orifice. At the extended, maximum-volume position, the motor is re-energized to repeat the cycle. Each cycle pumps a volume of air equal to the displacement of the piston-diaphragm assembly, and the cycle rate is largely controlled by the limiting orifice. Several sets of orifices are available, and the orifice is readily changed with a wrench or nutdriver.

The flow rate stability of the Model 808's was measured using the test

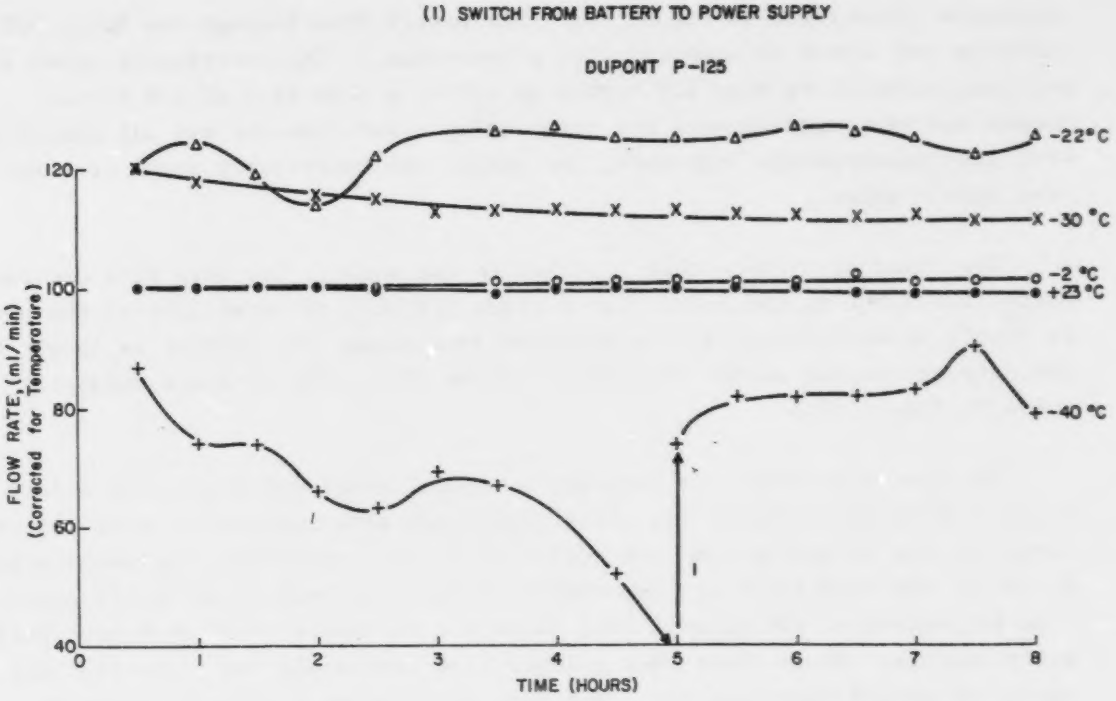

FIGURE 8. Flow rate stability, corrected for temperature, Model P-125.

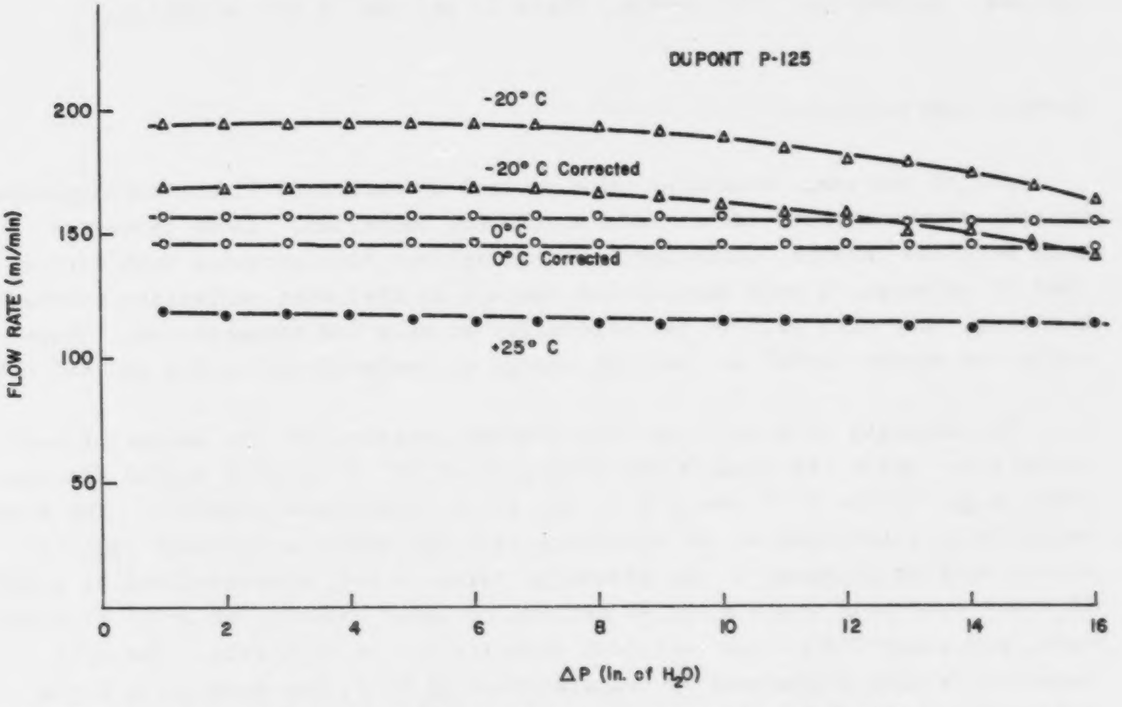

FIGURE 9. Flow rate versus differential pressure, Model P-125.

apparatus illustrated in Figure 10. (The sample flow through the Model 808 pulsates and cannot be measured with a rotometer.) The restricting valve was set independently to drop 1.5 inches of H_2O at a flow rate of 100 ml/min. Sample air was drawn through the restricting valve from the dry air manifold. When flow measurements were made, the sample was temporarily drawn from the soap bubble meter.

The limiting orifice that attaches to the pump is the only flow control option available to the user. For a given orifice, the stability of the pump is likely to be enhanced if the pressure drop across the orifice is larger than the drop across the sample collection medium (i.e., the pressure regulatory valve in Figure 10.)

The flow rate stability data for a typical Model 808 with a 100 ml/min orifice is shown in Figure 11. (The flow rates were measured at room temperature, but the values plotted are corrected to the respective test temperature.) At 25° C, the flow rates are reasonably uniform and tend to be within about 5 to 10 percent of 100 ml/min. The pumps did not operate for an 8-hour period at 100 ml/min. It is clear that a lower flow rate would tend to extend the operating period significantly. The pump operates on a periodic basis--a quasi "duty cycle"--in that the battery circuit is closed and the motor cycles the cam. During the "off" period, there is no load on the batteries.

BATTERY CONSIDERATIONS

All of the pumps evaluated were powered by secondary (i.e., rechargeable) sealed, sintered plate nickel cadmium (Ni-Cd) batteries. These batteries have very low internal resistance and can deliver high currents with little loss of voltage. A very significant feature is that when delivering moderate currents, they will perform satisfactorily at very low temperatures. These cells can supply useful but reduced energy at temperatures as low as -40° C (3).

The capacity of a Ni-Cd battery depends largely upon the manner of battery operation. Cells are usually characterized at 25° C and at a stated discharge rate; e.g., C/5 or C/10, where C is the rated ampere-hour capacity. The actual capacity is a function of the discharge rate and tends to decrease significantly with an increase in the discharge rate. A cell characterized at a C/5 (5 hour) rate will yield about 80 percent of rated capacity at a C/1 (1 hour) rate, and about 108 percent of rated capacity at the C/10 rate. The cell capacity is also influenced by temperature. At 0° C, for example, a Ni-Cd cell will deliver approximately 90 percent of its room temperature capacity (3).

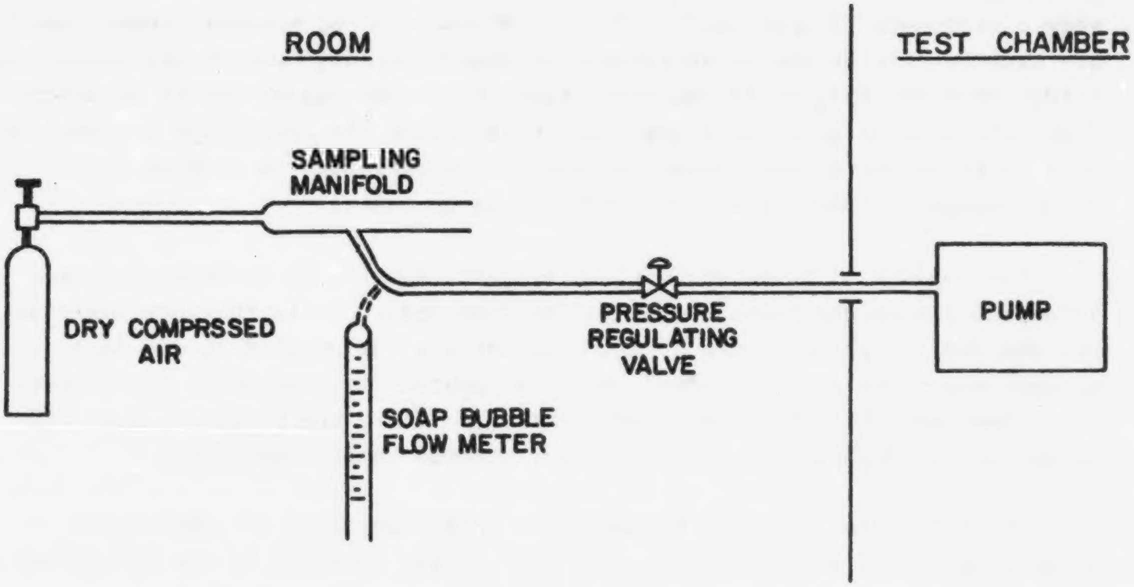
ROOM
TEST CHAMBER
SAMPLING MANIFOLD
DRY COMPRSSED AIR
PRESSURE REGULATING VALVE
PUMP
SOAP BUBBLE FLOW METER

FIGURE 10. Test apparatus for the Accuhaler Model 808.

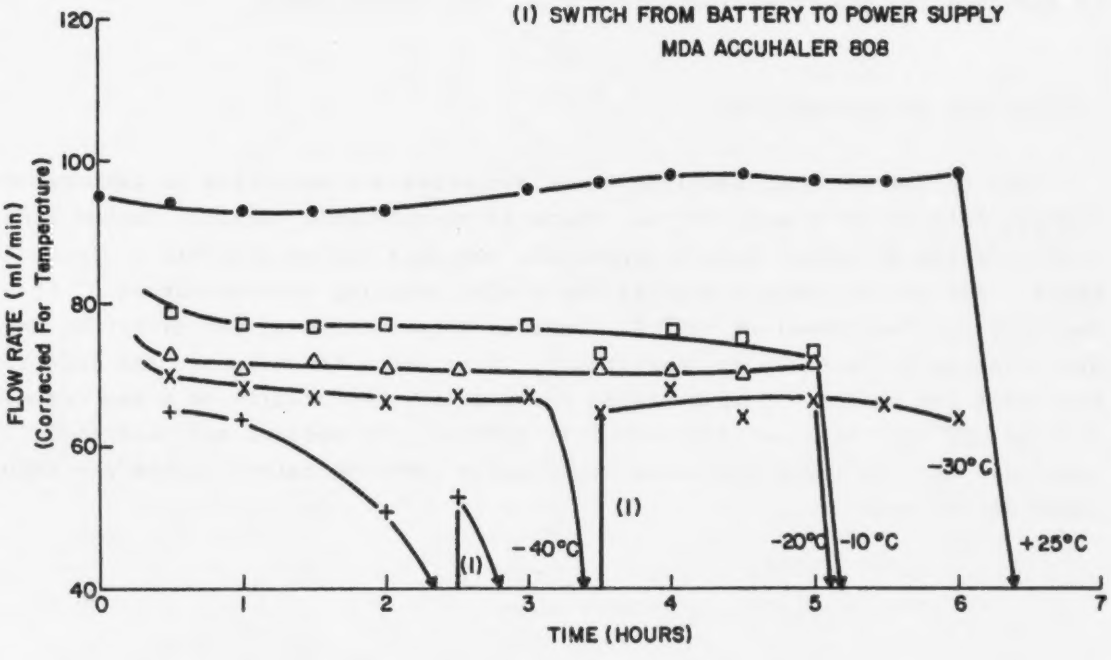

FIGURE 11. Flow rate stability, corrected for temperature, Model 808.

There is very little data available that is descriptive of the reliability, i.e., cycle-life, of Ni-Cd cells at low temperatures. Data that are available show a seriously reduced cycle-life at -18° and -34° C; however, these results are attributable to the establishment of unsatisfactory operational conditions rather than any failure to the cell itself (3). The reader should be mindful that many factors other than temperature influence the cycle-life and performance of Ni-Cd batteries. These include use factors such as routine depth of discharge, recharge practices, and discharge rates.

The results of these evaluations suggest that the Ni-Cd batteries used in personal sampling pumps yield good performances. While they are inadequate for the desired performances at low temperature, the problem is due largely to pump characteristics. Indeed, battery capacity is reduced at low temperature; however, the pumps demand more current. Thus, the batteries must discharge at the higher rate, which further reduced their capacities.

The battery pack should be used with care regardless of temperature. Recharging should be carried out with the charger supplied by the manufacturer according to instructions and at room temperature. In lieu of this option, the batteries should be charged at a constant C/10 rate for about 15 hours, or at a C/20 rate for much longer periods. (C is the ampere-hour rating of the battery.) The battery should not be recharged unless a significant portion of its capacity has been dissipated; e.g., C/3 ampere-hours.

SUMMARY AND RECOMMENDATIONS

All of the personal sampling pumps evaluated are sensitive to temperature changes between 25° C and -50° C. There is considerable variance in the sensitivity of the different models evaluated, and some variance within a single model. All of the pumps evaluated are useful sampling instruments at 0° C, and none are functional at -50° C. Between these extremes, the different models are affected differently by temperature. From among these pumps, the industrial hygienist can select a pump suitable for most any application to a low temperature of -20° C. At lower temperatures, however, the options are severely limited. For the pumps evaluated, reasonable low-temperature limits are tabulated as follows:

PUMP	LOW TEMPERATURE LIMIT (° C)
MSA Model G	-20
MSA Model S	-20
RAC Model 2392PS	0
MSA Model C-200	0
DuPont Model P-125	-30
MDA Model 808	-20

It should be emphasized once again that a comparison of the pumps evaluated was not an objective of this effort. The pumps are rated or specified differently by their manufacturers, and, consequently, comparison is somewhat unfair. Moreover, they were tested differently. This is especially true of the pumps which were not tested as CMDPSU units. However, there is an obvious quality of construction and room-temperature performance about some of these pumps which should be acknowledged. The MSA Models G and S, the MSA Model C-200, and the DuPont P-125 perform well at room temperature and give an impression of quality construction. The Model 808 has a different operating mechanism which could have some advantages. It should, for example, be relatively insensitive to battery status until the pump fails to operate at all. The Model 2392PS is similar in many respects to the Models G and S. It is lighter, has a smaller battery pack, and performs well for 8 hours at room temperature.

One objective of the evaluation effort was to evolve a set of recommended standards for personal sampling pumps for use in cold environs. We concluded, however, that the personal sampling pumps evaluated were not designed for use in sub-zero environments. Instead, they were designed and optimized for use in temperatures near 25° C. We conclude further that, in response to the solicitation for pumps for this evaluation, standard models were submitted without significant changes to optimize these units for low temperatures because of insufficient time and incentive. Consequently, standards based upon the results of these evaluations will tend to be premature and somewhat pessimistic. Standards recommended in the Final Report should be considered as preliminary, subsequent to further investigations and developments (1).

ACKNOWLEDGEMENTS

This study would not have been possible without the cooperative support of the manufacturers of the pumps evaluated. These manufacturers made pumps available for testing at no cost or risk to the authors.

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Discussion

TURNER: Bill Turner from Harvard. Were you able to make any pulsation measurements in any of your tests?

PARKER: No, we did not. One of the pumps that we looked at was very unique in that it had a critical orifice that controlled the flow. The pump exhausted the cavity of the diaphragm. The electrical system became inoperative at that point. It came to a stand position, and then a spring turned the diaphragm to its stand position, opening the cavity and drawing the sample through a critical orifice.

This pump had a very unusual pumping mechanism. It would take the sample, pull it through the orifice, and then recycle the diaphragm. But all these were tested at relatively stable constant flow rates.

Electrochemical Air Lead Analysis for Personal Environmental Surveys

Francis J. Berlandi, Ph.D., Gerald R. Dulude, Reginald M. Griffin, Ph.D.,
and Eric R. Zink, Ph.D.
ESA Laboratories, Inc.
Bedford, Massachusetts

INTRODUCTION

Exposure to lead via airborne particulates has become a cause of increased concern in the United States. The U.S. Government, via the Environmental Protection Agency, has recently proposed an ambient air lead standard of 1.5 μg/m (1). The justification for the enactment of this standard has been the increased lead exposure from both mobile and stationary lead sources by the general populace. This has been documented by the monitoring of blood lead levels in both children and adults in high- and low-exposure zones. The recommended method of measurement for determining air lead exposure is the collection of the air particulate material on a filter medium, as in the normal TSP methodology. The lead is then extracted from the filter into a solution and measured by a chemical technique.

Since 1968, the use of anodic stripping voltammetry (ASV) to measure blood lead levels in both children and adults has become quite widespread. Over 20 percent of the medical and clinical screening facilities in the United States use anodic stripping voltammetry as their major technique for blood lead analysis (2). This paper describes the use of a rapid electrochemical technique for the measurement of air lead using ASV.

The method (3) is summarized as follows. The air filter to be measured is placed in a test tube or another suitable container. The filter is soaked for 10 minutes in a Metexchange® reagent. The lead particulate is eluted and/or dissolved from the filter matrix with mechanical agitation. The sample reagent mixture containing both the solution and the filter is placed directly on the electrode assembly on the ESA Model 3010A Analyzer. The analysis sequence is initiated, and, approximately 90 to 150 seconds later, a quantitative measure of the amount of lead on the filter is available to the operator as a digital display. A permanent record is also available in the form of a recorder tracing.

The basic advantages of the technique include: a practical lower limit of measurability for lead in the 1 to 10 nanogram range; accuracy and precision which compares favorably to a standard reference technique; and a convenience of analysis which is both rapid and simple.

A GENERAL DESCRIPTION OF THE ASV TECHNIQUE

Anodic stripping voltammetry is an electrochemical technique involving two steps. The first step is the plating or reducing of metal ions into a mercury electrode by holding the electrode potential at a more negative value than is necessary to cause the reduction of those metal ions of interest. The potential of the electrode is then rapidly and linearly varied in a positive or anodic direction. When the potential of the test electrode reaches the formal potential of a metal ion/metal couple, that particular metal will reoxidize back into solution, and a current will flow in the measuring circuits external to the electrochemical cell. Because each metal has a unique formal potential, a number of different metals can usually be analyzed simultaneously.

Figure 1 is a simplified picture of the two-step process called ASV. In the first step, the metals are being reduced by holding the electrode at a controlled potential. If the metal ions were present in relatively high concentrations, it would be possible to quantitatively measure them during the reduction step by integrating the area under the current-time curve displayed in the top half of Figure 1. When dealing with parts-per-billion (ppb) metal ion concentrations, the contribution from reduction of all reducible metal ions present to the current-time integral is small (as represented by the cross-hatched area of the plot).

The major fraction of the current-time integral will be due to reduction of impurities (such as hydrogen ion) present in excess of the metal ions. If, at the end of the plating step, the potential of the electrode is varied in a positive direction, the current signal obtained will be almost entirely due to reoxidation of each reduced metal present in the electrode. This step is depicted in the lower half of Figure 1.

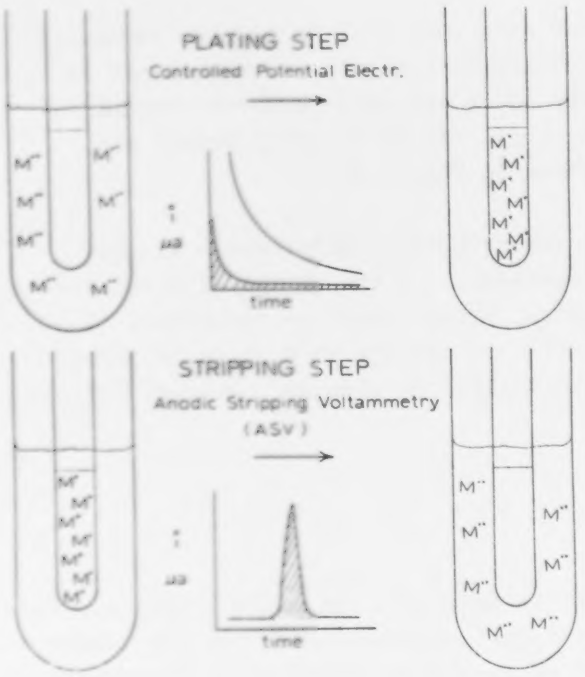
PLATING STEP
Controlled Potential Electr.
M⁺⁺
M⁺
i
μa
time
STRIPPING STEP
Anodic Stripping Voltammetry
(ASV)

FIGURE 1. Plating step and stripping step.

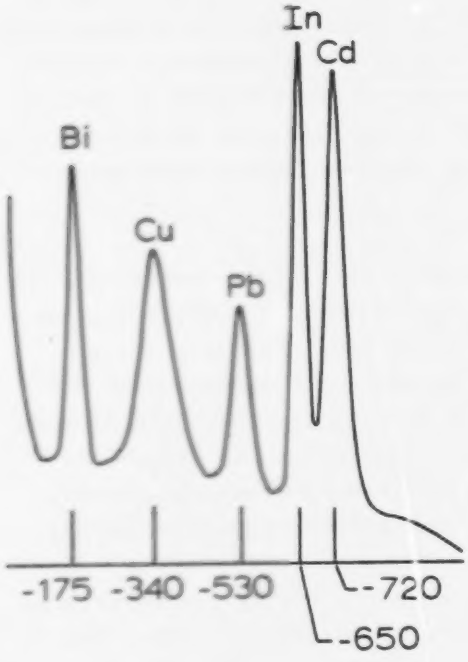

FIGURE 2. ASV scan.

matrix: 4F LiCl, 0.5F NaAc
pH: 4.5
plate pot'l: -1100 mv
plate time: 30 minutes
sweep rate: 60 mv sec
metal concentrations 20 ppb

Stripping Peak Potentials
vs. the Ag/AgCl reference

When the test electrode is composed of a thin film of mercury deposited on an inert substrate, such as the waxed graphite electrode, the result of the anodic stripping step will be a very sharp and well-resolved current peak for each metal deposited (into the thin film of mercury) during the plating step. A typical ASV scan is shown in Figure 2.

Peak potentials serve to identify the mercury-soluble metals in the sample. The height of each peak is proportional to the amount of metal ion reduced into the mercury and is, therefore, proportional to the amount of metal present in the sample. Figure 3 illustrates the kind of calibration curve linearity that is regularly obtained with the composite mercury graphite electrode (CMGE).

ASV AS A REFERENCE METHOD

Most analytical techniques (4) for air lead analyses require that the lead particulate be extracted, dissolved, or totally digested from the air filter matrix. The validity of the rapid, ASV analytical methodology is established by comparing the measured lead values from this new methodology to a second set of values obtained by using an EPA-recommended, acid extraction method on the same or duplicate samples. The EPA methodology is fully described in the Proposed Ambient Air Standard for Lead and is compatible with a final lead determination by atomic absorption on anodic stripping voltammetry. At this point, we define the ASV wet digestion as denoting an ASV analysis performed on conventionally digested samples, whereas ASV extraction will denote the rapid and relatively newer ASV techniques using samples treated with Metexchange® reagent.

Since most of the comparison data developed in this study compare the ASV extraction technique to the ASV wet digestion methodology (5), Table 1 summarizes the ASV wet digestion performance on standard NIOSH lead air filter sets from 1974 to 1977. The data demonstrate an excellent agreement of ASV wet digestion data with results obtained from a variety of other methods such as AAS and dithizone. Three years of comparison studies on ESA laboratory performance on both air filter and blood lead proficiency standards provide additional data as to the inherent validity of the ASV wet digestion method.

The ASV wet digestion methodology is also compared for agreement with AA results obtained on duplicate samples of extract from hi-vol filters. The summary of results is shown in Table 2. Based on the results shown in both

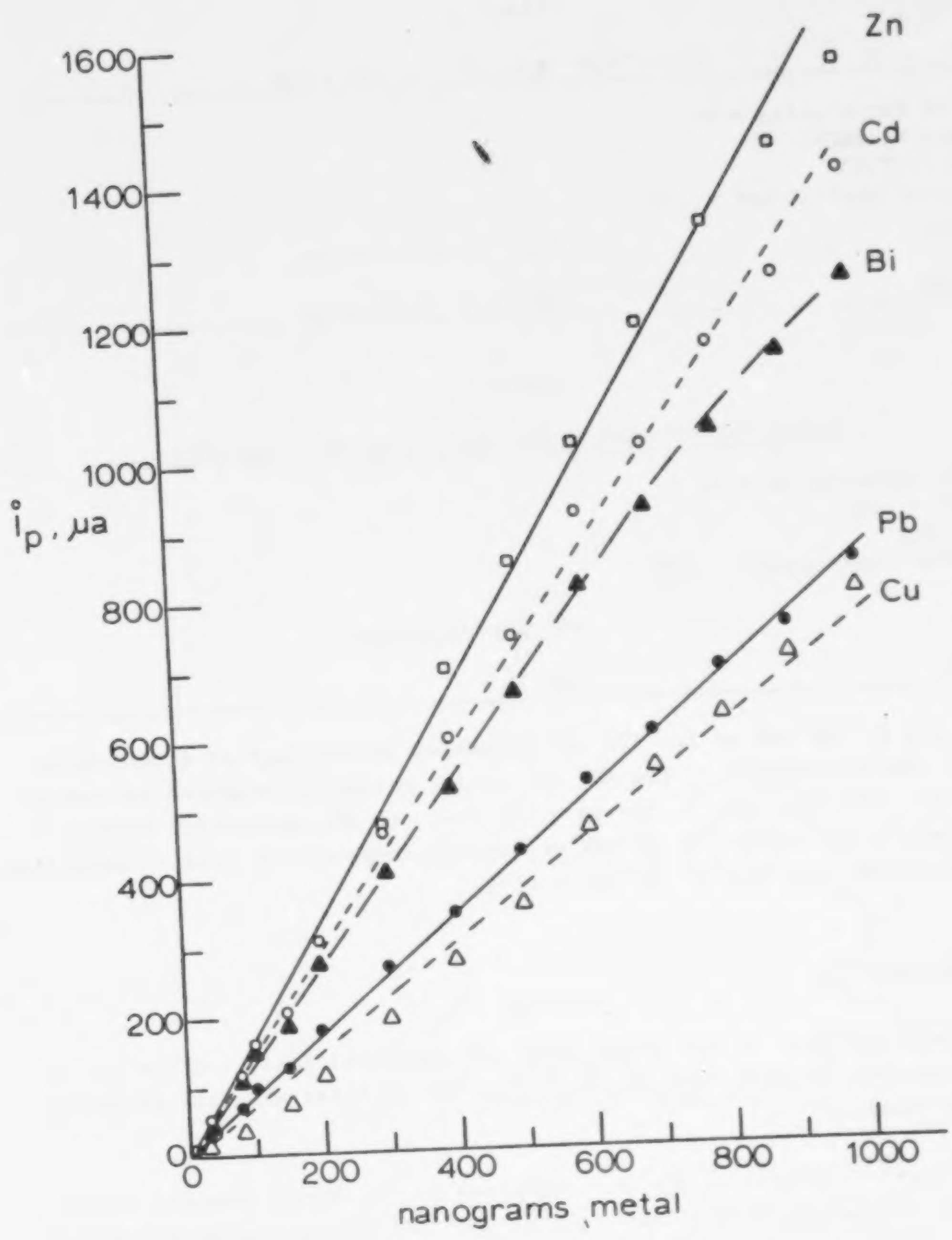

FIGURE 3. Typical ASV calibration curves.

TABLE 1

NIOSH "PAT" Summary for Air Lead

Number of value pairs = 64
Intercept = .00087
Slope = 1.01140
Correlation coefficient = .9914

$\bar{X}$ = .10057	"PAT" result average
$\bar{Y}$ = .10086	ESA reported average

TABLE 2

Hi-Vol Filter Results ASV Wet Digestion versus AAS

Number of value pairs = 20
Intercept = .235
Slope = .969
Correlation coefficient = .998

$\bar{X}$ = 12.65	ASV wet digestion
$\bar{Y}$ = 12.50	AAS

Tables 1 and 2, the use of the ASV wet digestion methodology as a reference method in the development of the ASV extraction screening approach is technically sound. In addition, it can be shown that the ASV extraction results can be compared to either AAS or ASV wet digestion-generated data to establish the validity and accuracy of the methodology.

AIR FILTER ANALYSIS

The previous section has established the technical basis for the use of ASV wet digestion in lead analysis for those not familiar with the electrochemical methodology.

This section summarizes the data obtained in the direct comparison of the ASV extraction air filter technique to both EPA filter standards and actual field samples.

Recovery of lead on air filters with this direct ASV extraction method was checked using EPA standard air filters against the atomic absorption technique. Results are shown in Table 3.

TABLE 3

EPA Filter Strip Comparison

EPA STANDARD FILTER	ASV EXTRACTION	AA
µg Pb/filter	µg Pb/filter	µg Pb/filter
0	0	0.1
115	108	110
300	284	270
400	409	365
675	695	595

TABLE 4

Industrial Environment Filter Study

Number of pairs = 12
Slope = .984
Intercept = .96
Correlation coefficient = .999

$\overline{X}$ = 73.17 ASV wet digestion

$\overline{Y}$ = 72.95 ASV extraction

TABLE 5

Oxide Dissolution Study

TIME	PbO	PbO_2	Pb_3O_4
1 min	89%	75%	64%
3 min	91%	98%	84%
6 min	96%	97%	96%
10 min	92%	97%	99%
15 min	99%	103%	97%

Also, air filter pairs were checked from an industrial collection site against total digestion procedures. Duplicate air particulate samples were collected from each of several work environments. In each case, the duplicate pairs were collected simultaneously with equal collection efficiencies. One filter was analyzed using the direct ASV technique, and one was analyzed using a total digestion ASV technique. Results are shown in Table 4.

Dissolution studies on the more common oxides of lead that could occur on the air filter matrix were evaluated. Measured amounts of PbO, PbO_2, and Pb_3O_4 were placed in Metexchange® reagent. The amount of lead dissolved versus time was measured at various time levels. Since the particulate size used in

TABLE 6

Volumetric Air Lead Calculations

	Air Concentration (μg Pb/m^3)				
TIME	0.1 μg/m^3 Filter	1 μg/m^3 Filter	10 μg/m^3 Filter	50 μg/m^3 Filter	100 μg/m^3 Filter
5 min	.001	.01	.1	.5	1.0
30 min	.006	.06	.6	3.0	6.0
60 min	.012	.12	1.2	6.0	12.0
8 hr	.096	.96	9.6	48.0	96.0

the study was greater than 50 microns, the results are a conservative estimate of the rate of dissolution for typical lead species found on a filter substrate. Table 5 summarizes this data. Dissolution was complete in 6 to 10 minutes.

Discussion and Results

The advantage of both the ASV wet digestion and ASV extraction to air pollution measurements is their ability to accurately measure lead down to a level of 1 to 10 nanograms. The implications of this statement can be seen in the namagraph of Table 6. Using a sample time of 5 minutes at an air flow of 2 liters/minute will provide the user with 10 nanograms of collected lead on the filter if the air lead level is 1 μg/m^3.

The utility of the ASV extraction, rapid lead screening technique is best demonstrated in a limited field study conducted using OSHA-type portable air samplers. The study was conducted on December 8 and December 9, 1977. The purpose was to derive data on the relative lead exposure to a typical suburban commuter during a typical work day. A series of samples were collected during the work-day period. The chronology is summarized as follows:

SAMPLE 1: Air sampling in suburban industrial facility in Bedford, Mass., adjacent to no known air lead sources except limited vehicular traffic.

SAMPLE 2: Air sampling during drive from Bedford to Winchester, Mass., during the evening commuter traffic.

SAMPLE 3: Air sampling during drive from Winchester to downtown Boston after major commuter rush hour.

SAMPLE 4: Air sampling at a professional society meeting held in a second-floor conference room of an office building in downtown Boston.

SAMPLE 5: Air sampling during drive from Boston to Winchester, Mass., in the midevening traffic.

SAMPLE 6: Air sampling during drive from Winchester to Bedford, Mass., on the following morning during commuter traffic.

The exposure study results are presented in Table 7 and demonstrate the flexibility of the analysis to respond to a variety of sampling times. The data also indicate the consistent air lead levels accompanying the driving segments of the day.

The results demonstrate that the lead exposure on this day during transit in a vehicle is much higher than the lead exposure measured in the suburban industrial facility or in the downtown Boston office building. Plans are underway to extend the effort to monitoring pedestrian and nondriving exposure to lead while in residence at various types of roadway conditions. Due to the inherent simplicity of the method, the onsite evaluation of lead exposure is possible using an ASV analyzer and an appropriate power source, although the data presented here represents laboratory analysis.

A second series of samples was obtained on February 28, 1978, and analyzed using a wet digestion methodology. The sample summary is as follows:

SAMPLE A: Air sampling during drive to Waltham, Mass., from Bedford on Route 128.

SAMPLE B: Air sampling during meeting in office building one-half mile from Route 128.

SAMPLE C: Air sampling during drive to Bedford from Waltham on Route 128.

TABLE 7

December Monitoring Study

SAMPLE	TIME	DURATION	LEAD EXPOSURE
1	1013	127 min	.04 $\mu g/m^3$
2	1710	30 min	4.90 $\mu g/m^3$
3	1755	40 min	4.40 $\mu g/m^3$
4	1835	145 min	.69 $\mu g/m^3$
5	2100	23 min	4.46 $\mu g/m^3$
6	0810	25 min	4.06 $\mu g/m^3$

SAMPLE D: Air sampling in office building in Bedford.

SAMPLE E: Air sampling during drive from Bedford to Winchester, Mass.

SAMPLE F: Air sampling during drive from Winchester to Cambridge, Mass.

SAMPLES G & H: Air sampling in two meeting rooms at MIT.

SAMPLE I: Air sampling during drive from Cambridge to Winchester.

SAMPLE J: Air sampling during morning commute, Winchester to Burlington to Bedford.

The exposure results are presented in Table 8 and show a similar pattern to the December exposure data.

This second set of data is consistent with the December exposures obtained using the rapid screen methodology. In both sets, the use of short-term samples to document the exposure during specific event periods provides the experimenter with a more accurate reconstruction of exposure events.

In conclusion, the sensitivity and convenience of the ASV rapid screen methodology offer extreme flexibility in the design and implementation of an ambient, air lead, field study program.

TABLE 8

February Monitoring Study

SAMPLE	TIME	DURATION	EXPOSURE	SITE
A	1114	17 min	3.2 $\mu g/m^3$	driving
B	1125	39 min	.9 $\mu g/m^3$	in bldg.
C	1210	12 min	9.2 $\mu g/m^3$	driving
D	1230	57 min	.5 $\mu g/m^3$	in bldg.
E	1625	24 min	4.7 $\mu g/m^3$	driving
F	1715	20 min	2.1 $\mu g/m^3$	driving
G	1745	79 min	.7 $\mu g/m^3$	in bldg.
H	1910	157 min	.4 $\mu g/m^3$	in bldg.
I	2200	30 min	3.8 $\mu g/m^3$	driving
J	0800	27 min	1.7 $\mu g/m^3$	driving

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Discussion

SCHEIDE: Gene Scheide, Environmetrics. In the automobile, did you use leaded or unleaded gasoline?

BERLANDI: I used leaded gas; we haven't gone to an unleaded car yet. I have a Volvo that is kept tuned up pretty well.

SCHEIDE: It would be interesting to compare to see how much emission you are getting from other vehicles on the road.

BERLANDI: Right. As I said, these are representative of a variety of driving conditions. I suspect that either I am entraining the dust, or it is coming from my car. I don't know. But certainly it is something that has to be investigated.

As I said, this is done on our own. We would certainly like to pursue this and do the study the way it should be done for documentation of this type of exposure.

CLIFFORD: Paul Clifford, Carnegie-Mellon University. If you are using a filter of 0.8 microns for a size cut, how much of the lead is smaller than that? How much of it are you missing?

BERLANDI: That is one thing that you have to remember about a 0.8 micron filter. It doesn't mean that particles less than 0.8 get through. The filter is sort of like a sponge. To my best knowledge, from the tests that I have run on particle entrapment, I think you are getting down to maybe 0.02, 0.01 microns.

People have tried bubbler techniques behind filters in order to capture the particle lead or any of the tetraethyllead. And from what they have been able to determine, 97 to 99 percent of the lead is captured on the filter in these cases.

CLIFFORD: So most of the combustion product of the tetraethylleads are actually very large?

BERLANDI: Yes. They can end up on the filter strip particles. Maybe someone else here would want to talk about vehicle exhausts. I am not an expert on it. But I know that those who have looked for the gaseous lead compounds, using the filter, have not seen significant transport to the interiors through the filter.

Studies of Semiconducting Metal Oxides in Conjunction with Silicon for Solid State Gas Sensors

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INTRODUCTION

This paper reports work at Carnegie-Mellon University dealing with semiconducting metal oxides, such as SnO_2 and ZnO, that hold promise as base materials for gas sensors. The research aims at the understanding of the role played by dopants properly selected to enhance the sensitivity of the materials; at the understanding of the mechanisms of electron exchange between bulk and surface when the gases to be detected are sorbed onto the surface; at the understanding of the transport of charge carriers; and at the understanding of the mechanisms involved in the preparation of the materials and devices, and the characterization of such materials and devices. The research purports to study the feasibility of materials' deposition and/or growth on conventional semiconductors, such as silicon. The work is being carried out by an interdisciplinary team from the Departments of Electrical Engineering, Metallurgy and Materials Science, and Chemical Engineering.

An integral part of this research program is work aiming at the understanding of the most prominent commercially available devices, and the incorporation of these devices and the devices emerging from our own research in a portable air pollution/combustible gas monitor. This part of the research is presented in a separate paper by D.T. Tuma and P.K. Clifford in these Proceedings.

This paper starts with a section on SnO_2 as a material for gas sensors.

Details of sample preparation by Radio Frequency Sputtering techniques are given, and analytical characterization of the SnO_2 thin films is described. The electrical characterization of the films, with a variation of the oxygen pressure within the sputtering ambient, is presented. A scheme is proposed which incorporates a stable SnO_2 film and silicon bipolar transistors in an integrated structure.

This paper proceeds with a section on ZnO as a material for gas sensors. It focuses on polycrystalline thin films and the strong dependence of film resistivity and gas sensitivity on grain size. The role of certain dopants in controlling the stability of the films and the gas sensitivity to certain gases is reported. Response times, reproducibility, and long-term stability of films investigated appear to be adequate.

The last section of the paper deals with H_2 and H_2S detectors utilizing MOS structures. These devices are Pd-SiO_2-Si Schottky barrier diodes and MOS capacitors. Both appear to be very sensitive to H_2 and H_2S.

A scheme is presented for incorporating Zeolite sieves on metal oxide devices for separating gases before detection by the sensor. This technique is also amenable for incorporation in Pd-SiO_2-Si devices.

SnO_2 AS A MATERIAL FOR GAS SENSORS

Sample Preparation

Thin films of tin dioxide are prepared by Radio Frequency Sputtering. The apparatus consists of a Randex 2400-J Sputtering system equipped with an He closed-cycle cryopump with variable power splitting facilities for the sputtering process. The target material is a sintered disc of SnO_2 prepared by pressing high-purity SnO_2 material obtained from Alfa Ventron Corporation.

A base pressure of 3.5×10^{-7} Torr is routinely obtained. The sputtering is performed by plasma composed of high purity (five 9's) argon and oxygen mixtures in dynamic equilibrium within the system. A water-cooled substrate table with tungsten-halogen lamps provides a deposition temperature range from about 120° to 450° C. The RF power supply is coupled to the anode (substrate)-cathode (target) assembly through a tunable impedance matching network. Typical RF powers for a deposition are in the range of 500 to 700 watts. Similar techniques are used for ZnO depositions.

Analytical Characterization of SnO_2 Thin Films

Sn and O_2 combine to form several compounds, some of which are SnO, SnO_2, and Sn_2O_3. The tetragonal structure of SnO_2 has a lattice structure given by a = b = 4.738 Å, and a c/a ratio of 0.675.

Films are analyzed for their morphology, structure, and composition. The Scanning Electron Microscope (SEM) and the Transmission Electron Microscope (TEM) complement each other in supplying information of grain size. In general, it is found that, for depositions carried out in an ambient of O_2/Ar at a pressure of 25 mTorr, the grain size is typically of the order of a few hundred angstroms.

Structural information is obtained from TEM and X-ray diffraction studies. The information from these data suggests that the films are polycrystalline in nature, with no particular orientation with respect to the plane of the substrate.

Elemental analysis of the films is carried out with the Auger Elemental Spectroscopy techniques (AES). The results are to be interpreted with caution because of the difficulties with the measurement system; however, preliminary results show that the Sn-to-O ratio for stoichiometric SnO_2 is about 1.60.

Figures 1 and 2 summarize the results of analytical characterizations on a SnO_2 thin film.

Electrical Characterization of SnO_2 Films

Figure 3 shows a plot of the room temperature measurement on as-sputtered films of SnO_2 with a variation of the oxygen pressure within the sputtering ambient. As can be seen, the films for 0 percent and 100 percent O_2 pressures (corresponding to 100 percent Ar and 0 percent Ar, respectively) possess high conductivities. The curve goes through a maximum in resistance, presumably at that point where the stoichiometric composition of SnO_2 is reached. More studies are underway to clarify this aspect.

Gas Sensitivity Response of SnO_2 Films

Several samples of SnO_2 have been studied for their response to oxygen and hydrogen. Studies with O_2 reveal information regarding chemisorption phenomena. The tests are carried out in a clean vacuum system that can be

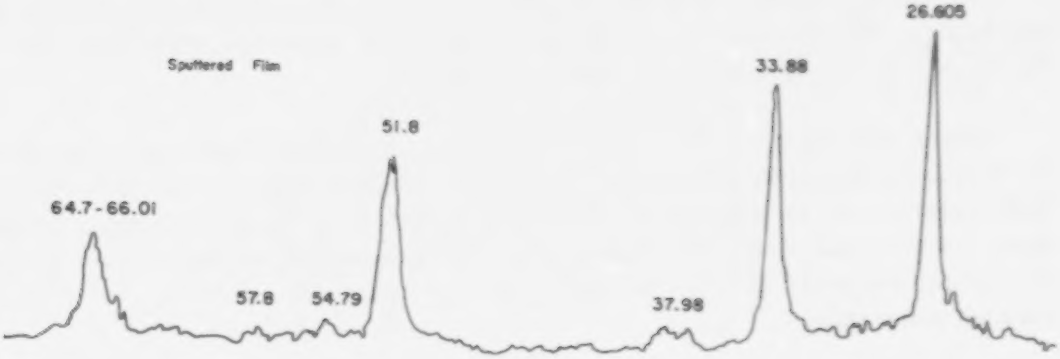
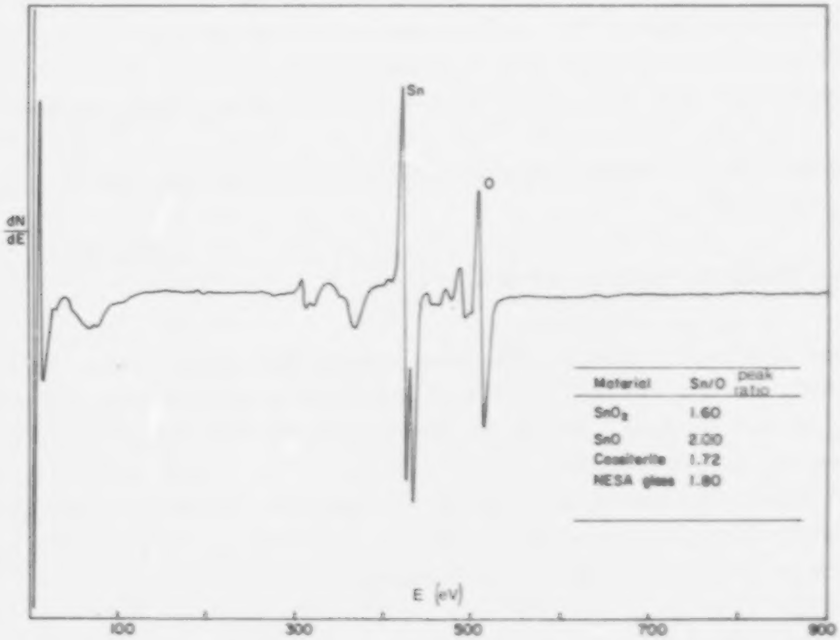
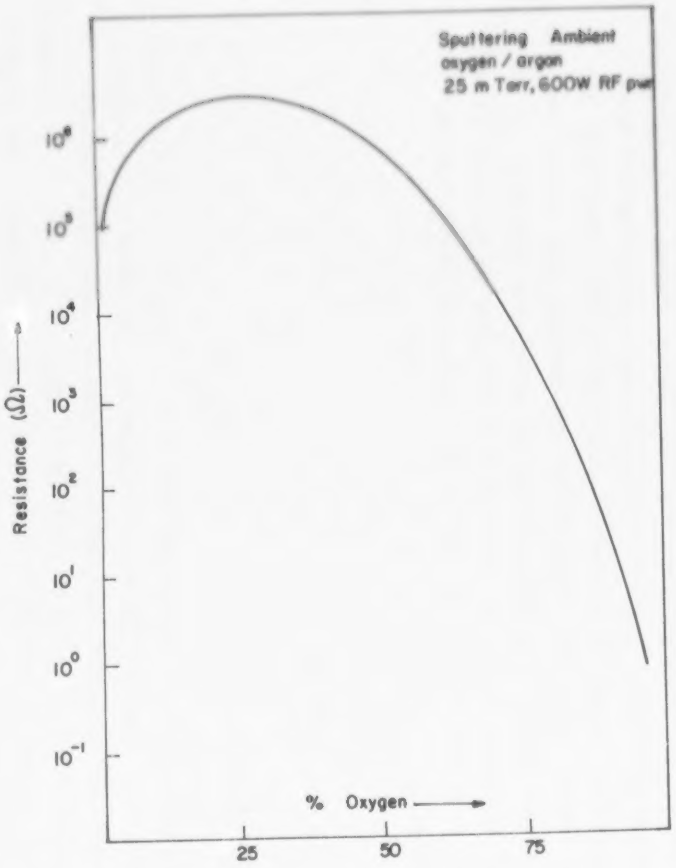


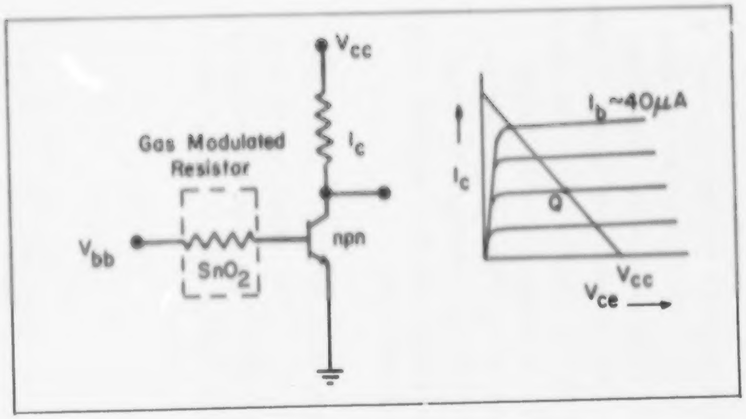
FIGURE 1. Typical X-ray diffraction pattern for a thin film of SnO_2. The figures correspond to the Bragg angles (2θ) as specified in the ASTM cards. The spread in the peaks is probably due to a strain in the lattice.



Material	Sn/O peak ratio
SnO_2	1.60
SnO	2.00
Cassiterite	1.72
NESA glass	1.80

FIGURE 2. Typical Auger spectrum of SnO_2. The relative ratio of Sn-to-O peak height remains substantially constant, although their absolute values differ from one region to another depending on the morphology. The table shows the relative ratios for various Sn/O combinations.




V_{cc}
Gas Modulated Resistor
I_c
V_{bb}
SnO_2
npn
I_b~40μA
I_c
Q
V_{cc}
V_{ce}

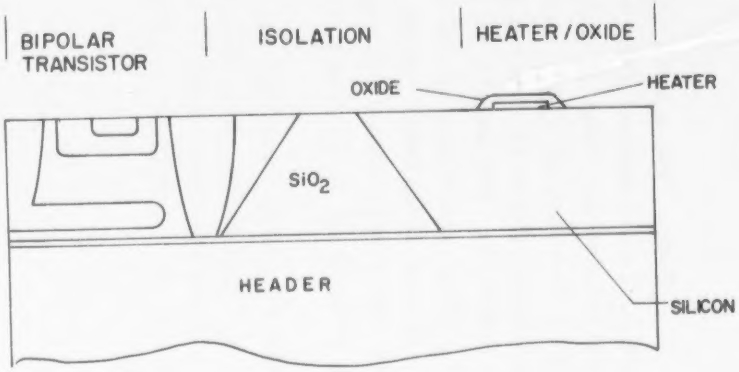

BIPOLAR TRANSISTOR
ISOLATION
HEATER / OXIDE
OXIDE
HEATER
SiO_2
HEADER
SILICON

FIGURE 3 (left). Variations of resistance of sputtered SnO_2 films as a function of the oxygen percentage in the sputtering ambient. FIGURE 4 (top right). The proposed integrated gas sensor. The SnO_2 serves as a gas-modulated base resistor that alters the quiescent level, and hence the output voltage. FIGURE 5 (bottom right). Bipolar transistor structure incorporating an isolation region for thermal shielding. The right-hand portion of the figure has a heater and the gas-sensitive oxide film. Figure used in computer study of heat analysis to evaluate the temperature distribution on the chip.

pumped down to 1 x 10^{-6} Torr. The sample is heated in this pressure range for an hour, after which O_2 is introduced into the system. Very precise amounts of the gas can be introduced by means of a special injection port. Readings of the resistance as a function of time, when plotted on semi-log paper, illustrate a linear dependence, which is typical of an Elovic plot. This, in turn, suggests a surface reaction. The sample is allowed to come to equilibrium in this environment, after which controlled amounts of H_2 are introduced in the system. A plot of the fractional change in resistance versus the preparation conditions of the sample shows increasing sensitivity for samples prepared in decreasing amounts of O_2 in the sputtering ambient.

However, stability studies show exactly the opposite effect. Thus, the most stable films are those prepared in 100 percent O_2. The opposing nature of these two results suggests that there is an optimum sputtering environment, which probably agrees with the optimum doping levels appropriate to the grain size of these films.

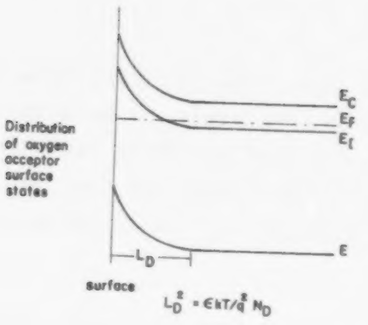
Devices

The results of the previous section indicate that some sacrifice can be made on the sensitivity of the films in order to considerably enhance the film stability. An increase in the sensitivity may, however, be made by coupling the film to an amplifying device such as a bipolar transistor. Figure 4 shows such a device, where it may be seen that the SnO_2 layer serves as a variable base bias to the transistor Q1. Figure 5 illustrates a prototype of such a device which is currently being developed in our laboratory. The need for integrating such a device calls for some isolation between the heater and the transistor. Such an isolation has been attempted with some success. A computer simulation of the heat transfer in such a device has also been carried out, suggesting the feasibility of the idea. We should be reporting on these aspects in short term.

ZnO AS A MATERIAL FOR GAS SENSORS

Polycrystalline Film Studies

Electrical properties of ZnO surfaces are very sensitive to ambient conditions, and high-purity, single crystal specimens are valuable for studying such processes. Gas-solid interactions by chemisorption processes involve charge transfer of electrons to or from surface layers. Figure 6 illustrates a specific example of oxygen chemisorption on n-type ZnO. Oxygen acts as an


Distribution of oxygen acceptor surface states
E_C
E_F
E_i
E
L_D
surface
$L_D^2 = \epsilon kT/q^2 N_D$

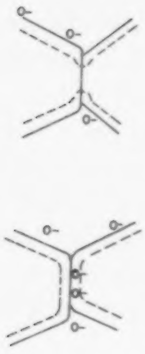


FIGURE 6 (left). Surface band bending in polycrystalline ZnO has a spatial extent of the order of a Debye length, L_D. FIGURE 7 (right). Conduction process in polycrystalline ZnO where adsorbed oxygen plays a role at the intergranular contact.

acceptor, introducing surface acceptor states that deplete electrons from the solid. The energy band bending depicted in this figure extends over a distance of the order of a Debye length, L_D, into the solid.

Conductivity measurements on single crystal specimens, however, will not reflect any surface sensitivity if L_D is small compared to the sample thickness. In polycrystalline films, the surface charge transfer process is still at play, and, with small crystallite sizes, the surface layers dominate the measured conductance. Figure 7 is an illustration of possible processes in polycrystalline films where individual grains are connected to form a conducting medium.

For the first situation, we show adsorption of oxygen at free surfaces. This establishes a depletion region accompanied by a large reduction in free charge. The depletion region can extend through the intergranular contact, as shown, pinching off the conduction path between grains. In the bottom figure, oxygen is adsorbed along grain contacts as well, resulting in a potential barrier to carrier flow between adjacent grains which is modulated by the amount of oxygen on the surface. The expression for the measured resistance of such films is

$$R_{meas} = g/n_{eff}q\mu_{eff}$$

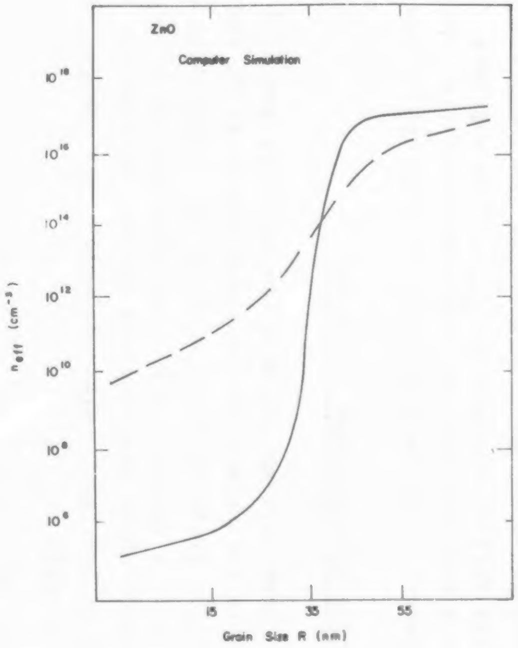
where n_{eff} is the effective carrier concentration in the individual grain, q is the electronic charge, μ_{eff} is the effective mobility in the intergranular region, and g is a geometrical parameter.

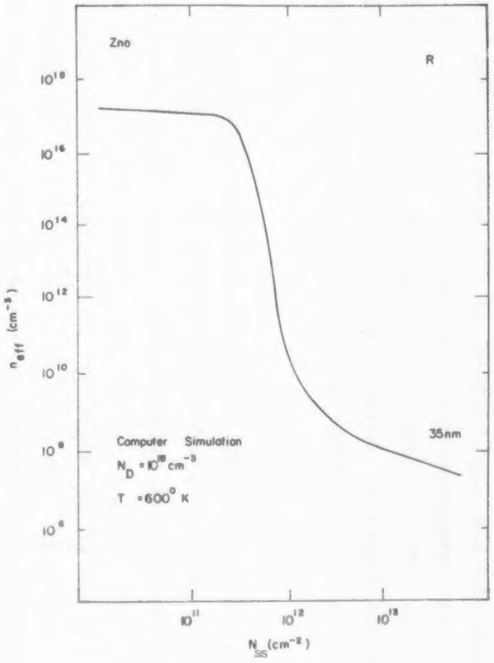
Studies by previous workers on films with this geometry have dealt with the situation by considering a highly conductive grain to be separated from its neighbors by a high-resistance phase which effectively determines the measured resistance. Such an oversimplification does not deal with the electronic processes directly, and cannot give more than qualitative information if applied to gas sensitivity.

A more fundamental approach recently applied to this situation has provided a semiquantitative description of electronic processes and a guide for materials processing to optimize gas sensitivity of polycrystalline metal-oxide semiconductors.

A chemisorption charge transfer model would be expected to depend critically on grain size and the corresponding number of free carriers taking part in conduction and surface reactions. For the case of small crystallites, the volume concentration of surface acceptors can be comparable to or even greater than the volume density of free carriers inside. Such a case requires simultaneous solution of Poisson's equation and the charge neutrality equation for each grain. We apply this approach to determine the crystallite surface potential, and, then, the effective carrier concentration as a function of the density of ionized surface acceptor states for a particular set of materials parameters (e.g., grain size and geometry, doping concentrations, donor and acceptor energy levels distributed in the bandgap, capture cross section for surface acceptor states, etc.) (1).

For the case of ZnO, the effective carrier concentration versus grain size is plotted in Figure 8 for a given surface acceptor density, N_{ss}. The results of the computer solution suggest the existence of a sharp transition in the effective carrier concentration between a highly conductive grain with a large radius and a nearly fully depleted grain of small radius. The transition occurs for small changes in grain size and, for a given doping level, is a function of temperature and concentration of surface acceptor states. The result suggests that material parameters might be adjusted such that small ambient induced changes in surface acceptor density could give rise to large changes in n_{eff} and the measured resistance of the film sensitivity. The





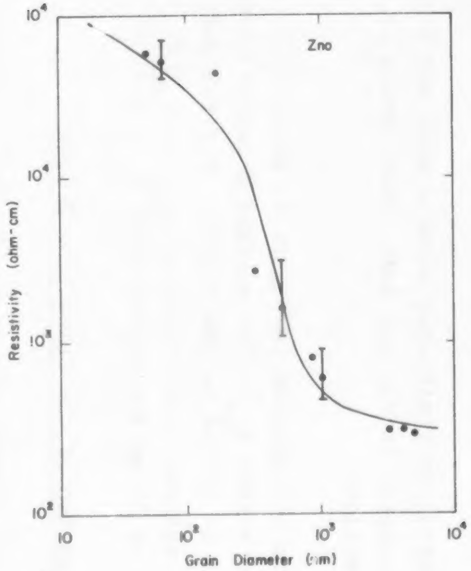


FIGURE 8 (left). Computer solution of effective carrier concentration in a single crystallite plotted versus crystallite radius. FIGURE 9 (center). Computer solution of effective carrier concentration plotted versus surface acceptor density on a single crystallite of ZnO. FIGURE 10 (right). Measured film resistivity of as-sputtered undoped ZnO versus diameter. After heating in air, all films have resistivity greater than 10^4 ohm-cm. Solid line is computer fit.

effect of a distribution in grain size about a mean and a distribution in energy of surface acceptor levels and bulk donor levels is shown to smear out this sharp transition.

The situation is illustrated in Figure 9, where n_{eff} (from the computer solution) is plotted versus N_{ss}. The surface acceptor concentration (for ZnO material parameters) is listed in the figure. For the particular material parameters used, an optimum sensitivity of n_{eff} to N_{ss} is determined for a discrete grain size of 35 nm and doping level $N_D = 1 \times 10^{17}$ cm^{-3}.

Experimental Confirmation of the Transition Region

In the effort to confirm the existence of a transition region in RF sputtered ZnO, and to justify the application of the model to gas sensitivity of these films, resistivity measurements were taken. Grain size of sputtered films was determined by TEM and SEM techniques. Grain size could be controlled by varying the film thickness or substrate temperature during deposition. The details of deposition and characterization of RF sputtered ZnO appear elsewhere (1).

Figure 10 shows data obtained for several films exhibiting the dependence of resistivity of as-sputtered ZnO on grain size. The data are fitted loosely to a computer-generated curve (solid line), where the fit was obtained for $N_D = 3.125 \times 10^{16}$ cm^{-3}, $E_C = .05$ eV, $N_{ss} = 2.2 \times 10^{12}$ cm^{-3}, and $E_A = 0.8$ eV. The Hall mobility could be measured in several of the lower resistivity samples. Its value was less than 1 cm^2/V-sec. Yeh (2) reports that the mobility in such films is independent of temperature and oxygen partial pressure, whereas n_{eff} changes with these parameters. We therefore infer that the measured resistivities reflect changes in n_{eff}. This suggests that the data of Figure 10 provide a semiquantitative confirmation of the dependence of the effective carrier concentration on grain size in polycrystalline ZnO.

Gas Sensitivity Testing of Sputtered ZnO Films

Gas testing has been carried out with the specific goals of 1) evaluating the feasibility of this technology for personal monitors; 2) establishing optimal film doping and/or grain size; 3) determining sensitivity as a function of temperature for various gases; and 4) exploring the use of additives such as palladium or platinum which are known to enhance sensitivity to particular gases. The response to hydrogen, carbon monoxide, and changes in the nitrogen/oxygen ratio, are measured.

Hydrogen testing is carried out by passing a mixture of forming gas (5 percent H_2, 95 percent N_2) and synthesized air over the sample. Concentrations in the range 0 ppm to 9,000 ppm are employed. Carbon monoxide testing at present is conducted under static conditions, using concentrations in the 100-ppm range. The nitrogen/oxygen ratio is varied from 100 percent N_2 to 100 percent O_2. In all cases, the film temperature is monitored with a chromel-alumel thermocouple. Film resistance is measured using an AC voltage and current; the AC technique is necessary because of the high thermoelectric power of ZnO, which results in sizable DC thermoelectric voltages.

The resistance measurement is performed with an AC digital voltmeter. However, a DC voltage proportional to the sample resistance is also derived and recorded with a pen recorder.

Figure 11 shows the hydrogen response of two Ga-doped ZnO films which were both sputtered onto substrates heated to 480° C. Both films are seen to quite closely follow a dependence on the square root of hydrogen concentration, i.e.,

$$\frac{\Delta G}{G_o} = A\ [H_2]^{1/2}$$

where G_o is the conductance in air and A is a constant. Therefore, calibration of a particular sensor is reduced to specification of the constant A for that device. Comparing the two curves of Figure 11, it is seen that Device B has a somewhat greater sensitivity. This device is similar to A, except that a 500 Å film of palladium was sputtered onto the ZnO film in the last step of fabrication. In Device B, palladium is probably acting to catalyze the dissociation of hydrogen--a necessary step in the reaction of hydrogen with the sensor surface. Based on the scatter in the data, a detection limit of 10 ppm H_2 is indicated for Device B.

The response of a sensor to hydrogen is indicative of the response of the device to a number of gases containing hydrogen; i.e., CH_4, H_2S, and NH_3. In these cases, the parent molecule undergoes dissociation, neutral hydrogen is produced, and the latter reacts with the sensor surface. Of particular practical interest are detectors for CH_4 and H_2S. In the latter case, a palladium device similar to Device B is particularly attractive, since palladium is known to catalyze the dissociation of H_2S (see below). However, ZnO devices must be protected against direct exposure to sulphur compounds, which poison this material by forming surface ZnS layers. Two solutions to this problem are

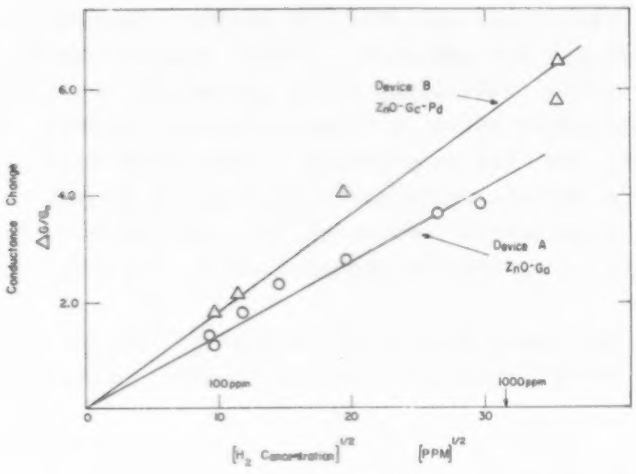


FIGURE 11

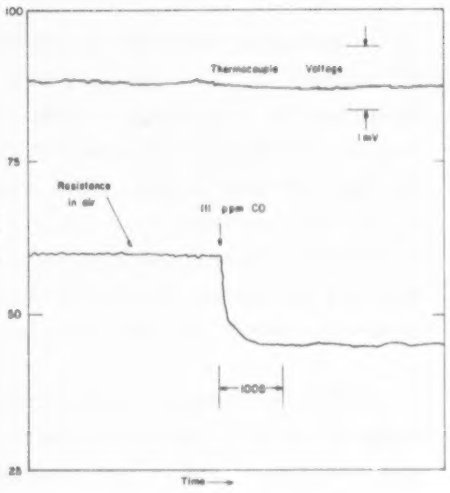


FIGURE 12

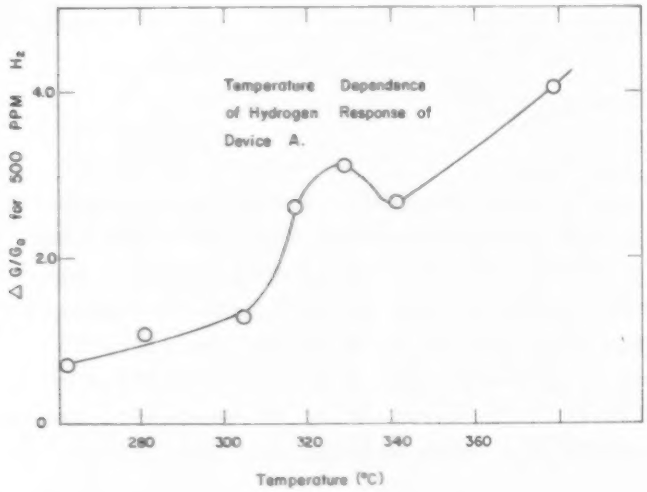


FIGURE 13

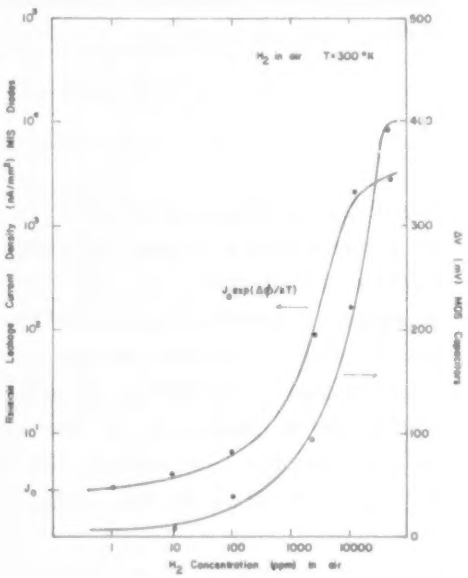


FIGURE 14

FIGURE 11. Hydrogen response at 330° C. FIGURE 12. CO response of Device A at 330° C. FIGURE 13. Temperature dependence of the hydrogen response of Device A. FIGURE 14. Reverse leakage current density of a Pd MOS diode and flat band voltage of a Pd MOS Capacitor plotted against hydrogen concentration.

being evaluated. One involves the use of a Zeolite molecular sieve (see below) over the film. The Zeolite is chosen to allow passage of hydrogen but not sulphur. Palladium is added to the outer layers of the Zeolite through sputtering or other means such that the dissociation of H_2S is promoted. Since this device will also respond to hydrogen, it must be paired with a device not sensitive to H_2S, but instead to hydrogen. The latter could be a Zeolite-covered film without palladium added to the Zeolite. The other solution being investigated involves cladding the ZnO film with palladium, which is relatively unaffected by sulphur compounds and which is transparent to hydrogen. In this case, the palladium acts to screen out sulphur.

Figure 12 is an example of the response of Device A to 111 ppm CO. Device B showed negligible response to CO, presumably because the overlaying Pd film prevented the CO molecules from reaching the ZnO film. Palladium or platinum additives, therefore, are useful for detectors designed to respond to small concentrations of methane or other gaseous hydrocarbons in the presence of large concentrations of CO.

In addition to the selectivity afforded by catalytic additives, the temperature-sensitivity relationship may be a means of enhancing selectivity. Figure 13 shows the temperature dependence of the hydrogen response of Device A. The temperature dependence is believed to be a unique characteristic of a particular gas. In the case of hydrogen compounds such as CH_4 or H_2S, the temperature dependence will reflect dissociation of the parent molecule, as well as reaction of the film to hydrogen, and, therefore, should be unique for a particular gas. Use of temperature as a means of selectivity will require processing information from an array of sensors operating at different temperatures. This approach is favored over scanning a single sensor through a temperature range because of response time considerations.

The response time, reproducibility, and long-term stability of films investigated thus far have been adequate for most monitoring applications. The response time for exposure to a gas is on the order of seconds; this measurement may reflect the response of the gas testing system itself and is therefore an upper limit of the film characteristic. Recovery following removal of the gas appears to be somewhat slower, with the present sensors requiring several minutes. Stability has been investigated over periods of 1 week, and the conductance in air of a given film appears stable within a 10-percent range for a film cycled over a range of temperature and exposed to a number of gases. Long-term stability is, of course, critical to the successful operation of gas sensors.

H_2 AND H_2S SENSITIVE MOS STRUCTURES

Schottky Barrier Diodes and MOS Capacitors

Thin metal films which dissociatively dissolve H_2, such as Pd and Pt, have been incorporated in integrated diodes and capacitors on passivated silicon substrates (3,4). Changes in work function at the metal-SiO_2 interface induced by ionized H_2 and gases such as H_2S and NH_3 can give rise to large changes in the reverse leakage current of a Schottky barrier diode or changes in the flat band voltage of MOS capacitors. H_2 sensivitity is shown in Figure 14 with the structures operated at room temperature. The figure illustrates diode sensitivity in terms of changes in reverse leakage current and changes in capacitor flat band voltage versus hydrogen concentration. One to 10 ppm H_2 in air are detected, with the upper limit on sensitivity being near 1 percent H_2.

MOS capacitors can be operated at elevated temperatures, which improves response times while the sensitivity to H_2 is preserved. Both structures are sensitive to H_2S, but operation at room temperature results in a short-term deterioration in response due to sulfur poisoning of the metal surface. However, the sensitivity is entirely reversible at elevated temperatures above 160° C in air. Diode structures cannot be used at elevated temperatures, whereas MOS capacitors essentially retain their characteristics in this temperature range. As an alternative to measurements of changes in flat band voltage with H_2 or H_2S, the actual change in capacitance can be measured at a given gate voltage. Figure 15 illustrates the result of such a measurement. The figure shows a change in differential capacitance versus H_2S concentration at elevated temperature in air. One to 10 ppm H_2S can be determined. Device sensitivity can be improved by minimizing the SiO_2 dielectric thickness.

Device Selectivity

The aspect of selectivity has been approached from several angles. Figure 16 constitutes a specific illustration where the addition of a catalyst as an impurity shifted the ZnO temperature distribution for the response of the film in the case of CO. In general, the sensitivity of a metal-oxide is temperature dependent, and conceivably an array of devices operating at different temperatures with the associated signal processing could be used to discriminate several gas constituents. Alternatively, preprocessing of the gas ambient by filtering of the gas components--analogous to preprocessing

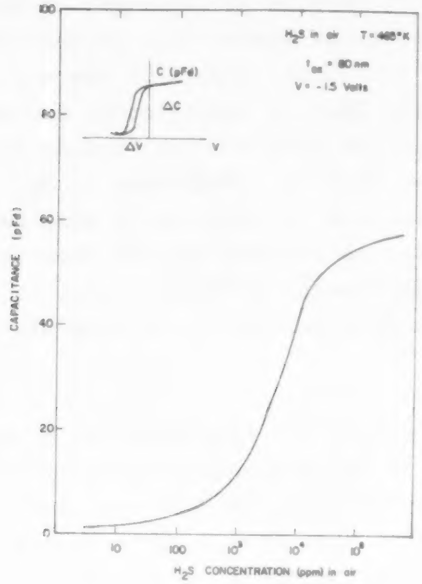


FIGURE 15

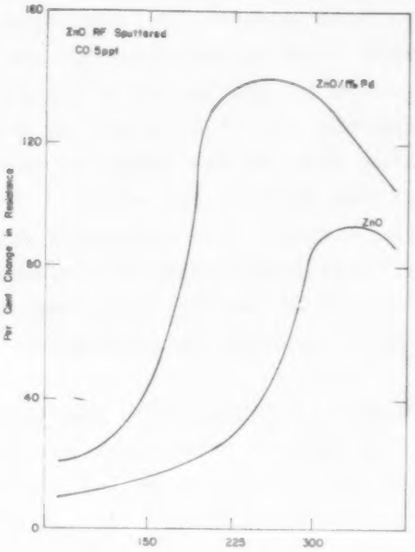


FIGURE 16

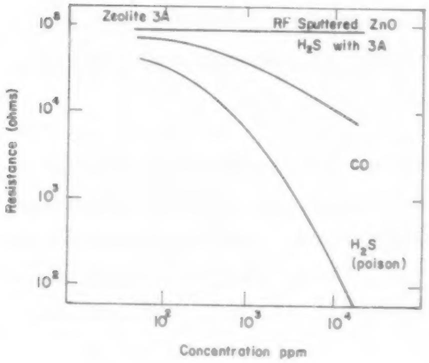


FIGURE 17

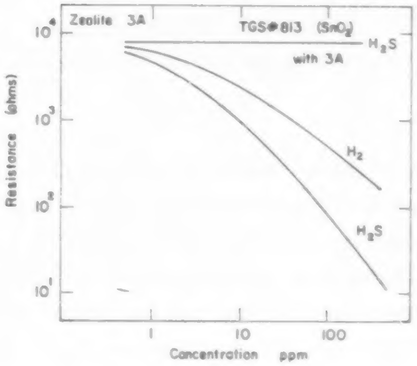


FIGURE 18

FIGURE 15. Differential capacitance in a Pd MOS capacitor plotted versus H_2S concentration for a negative gate bias of -1.5 volts. FIGURE 16. Percent change in resistance of ZnO film exposed to CO in air plotted versus temperature. The presence of Pd in the film acts to shift the temperature dependence of the response to lower temperatures. The sensitivity is improved. FIGURE 17. 3 Å pore size Zeolite incorporated on ZnO sensor effectively screens H_2S separating the response to H_2 and CO from H_2S. FIGURE 18. 3 Å pore size Zeolite on SnO_2 is also used to separate H_2 from H_2S.

of communication waveforms before detection--can provide selectivity, as well. We have been working to incorporate Zeolite molecular sieves with commercially available devices and with our own integrated versions. Figure 17 demonstrates the results of the use of a 3 angstrom pore size Zeolite deposited on ZnO as a filter for CO. H_2S, which is a poison to ZnO, is screened out because its molecular size is too large to pass through the Zeolite. Responses to H_2S without the Zeolite are shown. With the filter, H_2S is effectively screened from the sensor. The currently employed deposition process for the Zeolite is not fully compatible with standard planar processing techniques and, before this technology can be fully implemented, thin film deposition of molecular sieve material must be developed.

Figure 18 illustrates the utility of 3A Zeolite for separation of H_2 and H_2S. The results shown here are for a commercially available SnO_2-based detector. Two identical detectors, with one incorporating the Zeolite, can effectively discriminate the response to H_2S from that to H_2. This is also of interest for the diode and capacitor structures referred to earlier.

CONCLUSIONS

Radio Frequency Sputtering is a powerful, versatile technique for the preparation of thin films of SnO_2 and ZnO to be used as sensors for certain gases.

In conjunction with SnO_2, the fractional change in resistance versus the preparation conditions shows increasing sensitivity for samples prepared in decreasing amounts of O_2 within the sputtering system. However, the most stable films are those prepared in 100 percent O_2. Thus, there appears to be an optimum sputtering environment for both a reasonably stable, and yet an adequately sensitive, film.

Reasonably stable films of SnO_2 (albeit not very sensitive) may be incorporated with bipolar transistors in an integrated structure, with the gas-sensitive portions being operated at elevated temperatures while the bipolar transistor remains at near room temperature.

In polycrystalline films of ZnO (and also SnO_2), the grain size depends on deposition temperatures. There appears to exist an optimum grain size for which the sensitivity of the film is significantly enhanced.

Ga doped ZnO films are stable, and with the addition of Pd can be used for the detection of H_2 and hydrogen bearing gases (CH_4, H_2S, NH_3) with good sensitivities. In the case of H_2S, the ZnO must be protected against direct exposure to sulfur compounds which poison the material.

In addition to the selectivity afforded by catalytic additives, Ga doped ZnO devices can be designed to operate at elevated temperatures, so as to have an enhanced sensitivity to gases.

Schottky barrier diodes and MOS capacitors, both incorporating Pd-SiO_2-Si layers, can be utilized as very sensitive H_2 and hydrogen-bearing gases such as H_2S and NH_3. In the diodes, their reverse current sets a limit to the maximum temperature of operation. The capacitors, however, can operate at sufficiently high temperatures (of the order of 160° C) so that the molecule of the detected gas may be dissociated.

Zeolites molecular sieves may be incorporated in the devices above to afford selectivity--by acting as filters against certain gases while passing some others which would dissociate on the surface and modulate the electrical properties of the sensor.

ACKNOWLEDGEMENT

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Discussion

MAGE: I would like to ask that the questions about this paper be held until after the next paper, because it will be on the same topic from the same department.

(NOTE: The discussion for this paper appears following the text of the next paper, "Microcomputer Control and Information Processing Technology for Semiconductor Gas Sensors.")

Microcomputer Control and Information Processing Technology for Semiconductor Gas Sensors

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INTRODUCTION

A primary goal of our research is the eventual development of a portable pollution monitor. The ideal monitor would be small, lightweight, safe, rugged, inexpensive, and capable of continuous operation throughout the workday. As a gas-detection system, it would need to respond reliably to combustible and polluting gases over a dynamic range of several orders of magnitude, with a time resolution of a few minutes and reasonable sensitivities determined by flammable and toxic limits.

A gas-detection technology that seems suited to the eventual fulfillment of these goals is that of semiconductor detectors. However, to date, semiconductor detectors have been characterized by low reproducibility, drift, and very poor gas selectivity. These limitations cannot be overcome until much more is known about the nature of the detection mechanism in the semiconductor material. Some of these limitations, however, appear to be inherently tied to the nature of the materials used in such a way that it is unlikely that they will be completely overcome by materials research in the near future. Although we will see the rapid evolution of a wide variety of semiconductor sensors in the near future, they will remain broad-spectrum devices. Aside from this lack of selectivity, it is likely that semiconductor sensors will continue to exhibit highly nonlinear responses which are not amenable to present "direct reading" instrument design.

If the computational power which is now becoming available at low cost in microcomputers can be used to compensate for the imperfections of present solid-state detectors, then the development of a portable gas-detection instrument may be possible. "Smart" instrument design through the use of microprocessors may obviate the need for a simple linear response and provide a means to enhance selectivity of existing or future detectors. This is made possible only by the significant decrease in both size and cost of computer systems over the past few years.

At Carnegie-Mellon University, we have been empirically investigating the basic response mechanisms of semiconductor detectors. That is, we determine the dependence of the semiconductor material properties on temperature, gas concentrations, fouling, past history, etc. The purpose of this investigation is twofold. First, we seek to provide insight into the characteristics which would be desirable in future detectors, thereby aiding in the development of higher-performance detectors. Secondly, we are determining which properties of the sensors are able to be exploited, by using innovative signal-processing techniques, to overcome their seemingly inherent limitations. A synergistic cooperation between semiconductor and microcomputer, broad-spectrum sensors and computational selectivity enhancement, may be necessary to make the genesis of a truly personal, portable gas-detection system feasible.

Instrumentation Design

The design of personal detection systems to date has concentrated on direct reading sensors with a simple linear response. They are most suitable to portable technology. Unfortunately, direct reading sensors are not available for the plethora of environmental contaminants which need to be monitored; the gap between specific sensors and monitoring needs is widening. For this reason, instrumentation design will need to adapt its methods to sensors of low gas specificity and nonlinear responses. Fortunately, this is possible with the advent of miniaturized computers. A microcomputer-based detection system would have the following attributes which may become indispensable in a portable personal gas monitor.

Display. An instrument for hazard detection would need to provide a warning signal when a dangerous level of a particular pollutant is present. A microcomputer could provide a hazard signal when either an instantaneous dosage or cumulative exposure exceeds a preset level. The threshold levels could be easily programed and may even be allowed to depend on other gas concentrations. In addition to warning alarms, a microprocessor-based instrument could be easily interrogated by the wearer to provide a display on demand of instantaneous, average, and cumulative exposures to one of several gases.

Memory. Increasingly, the focus of personal pollution monitoring is shifting from hazard detection to trace gas monitoring. For this, automated data analysis and data recording is needed to permit the handling of the large amounts of data generated during routine monitoring. We need an instrument not only capable of direct gas analysis and small enough to be carried by a worker, but it must also maintain a memory of gas exposure throughout the day. This memory can then be transferred to a permanent record in a centralized monitoring system. Such a personal monitor necessitates the use of microprocessor technology with its attendant semiconductor memory. Present processor technology enables us to visualize an instrument small enough to be carried which would provide a hazard signal if one of four or five gases exceeded safe levels, and which could maintain a memory of the day's profile of gas concentrations. At the end of the day, that memory could be dumped into a larger computer facility, providing permanent and detailed records of personnel exposures.

Control. A microprocessor's capability for real time control extends from the mundane to the esoteric. At one level, the microprocessor may be used to reduce power consumption by intermittently operating the sensors. Sensors may be sampled automatically, with power-conserving dead space between samples. More interestingly, the interactive control of semiconductor sensors may extract much more information from the sensor than could be had statically. Feedback to and control of the electrical bias point or device temperature, based on computed results, may be needed to optimally exploit the semiconductor's detection properties.

Signal Processing. Information from a bank of sensors--each sensor of which in itself is unselective but exhibits differing relative gas sensitivities--can produce a system of nonlinear equations. These may be solved numerically by a computer. Microcomputers having the computational ability and memory for a task such as this (i.e., nonlinear regression of sensor information to produce gas concentrations), are now available in sizes and costs amenable to the needs of personal dosimetry. Current trends in processor technology indicate that their signal processing abilities might well continue to grow; increasingly complex algorithms may be implemented in real time.

SELECTIVITY ENHANCEMENT

Differential Sensitivities

Sufficient information must be provided to the microprocessor so that it is able to deconvolve the gas concentrations of interest. This may be done either by using several detectors with different relative sensitivities to the gases, or by using one sensor whose sensitivities to the gases may be changed in time by computer manipulation of a controlling parameter. The following methods may be used to gain differential sensitivities from otherwise broad-spectrum sensors.

Detector Construction. Gas detection by semiconductor sensors is a complex process involving absorption and desorption of gases on the semiconductor surface, surface chemical reactions, diffusion of gases along grain boundaries, and interaction of adsorbed species with the electronic structure of the material. Layer thickness, grain size, heat treatment, dopant concentrations, and any physical or chemical modification of the catalytic activity of the surface may be used to change gas sensitivities. Although it may be difficult to attain--for example, absolute selectivity by a change in dopant concentration--at least the relative sensitivities to several gases may be sufficiently changed to allow use of the device.

Filtering Techniques. Various filters may be used in conjunction with wide-spectrum, metal oxide semiconductor detectors to render very different relative gas sensitivities. In particular, we have had success with Zeolite molecular sieves. This technology may be merged with silicon integration techniques to yield single chip sensors composed of a dozen or so differently filtered, metal oxide semiconductor devices. Such ultra-miniaturization may soon produce a very powerful, general-purpose personal gas monitor.

Manipulation of Bias Conditions. Some semiconductor gas detectors (e.g., Pd-SiO_2-Si Schottky diodes) have electrical bias conditions which may be made subject to microcomputer control. Depending on the physical and chemical properties of the particular gas species being adsorbed, a change in bias of the semiconductor device may change its gas sensitivity. Hence, a change of electrical bias by the microprocessor yields different relative gas sensitivities. Simplicity of control, rapidity of response, and ease of interfacing, make electrical bias change a desirable form of control. Unfortunately, there are few sensors which behave reproducibly and whose relative gas sensitivities have yet been reliably measured.

A semiconductor gas sensor's thermal bias--its temperature--is subject to easy manipulation. Because the mechanisms of chemisorption, gas diffusion, chemical reactions, and gas-bulk electronic interaction are all strongly temperature-dependent, a metal oxide semiconductor's sensitivity to a gas is a very strong function of temperature. A single sensor, if operated sequentially at several temperatures, will exhibit different relative gas sensitivities. Each gas will have its own "eigenfunction" of sensitivity relative to temperature. By changing the temperature of a device, a processor may gain enough independent sensitivities for the determination of several gas concentrations.

Development of the Detection Algorithm

After a bank of sensors exhibiting different relative sensitivities to gases has been assembled by any of the above techniques, signal processing can be used to deconvolve the individual gas concentrations from the collective response of the sensors. To construct the deconvolution algorithm, a knowledge of the exact nature of the response of all the detectors to all the gases is needed. Quantitative expressions of detector response can be determined empirically, guided by theoretical knowledge of the reaction mechanisms and a suitable experimental data base. It is important to note, however, that a full understanding of a device's nature is not necessary for using that device. A phenomenological knowledge of its behavior, derived empirically, is sufficient. The microprocessor has the benefit of a collection of responses either gained from a bank of sensors or a single sensor whose operating conditions are changed sequentially in time (or any combination thereof):

$$S_1 = f_1 (G_1, G_2, \ldots G_n)$$

$$S_2 = f_2 (G_1, G_2, \ldots G_n)$$

$$\cdot \quad \cdot \quad \cdot$$

$$S_m = f_m (G_1, G_2, \ldots G_n)$$

where S_i is the response in voltage or current;

f_i is the predetermined functional dependence of response on gas concentration; and

$G_1 \ldots G_n$ are the concentrations of ambient gases.

If $m \geq n$--that is, if there are enough detector responses with different relative gas sensitivities--then the gas concentrations, $G_1, G_2, \ldots G_n$, can be determined. Of course, the f's will not in general be linear functions, and the above system of equations will not be explicitly solvable analytically. Numerical techniques, however, can be developed and used to solve such a system. The efficiency of those techniques will depend on the specific nature of the nonlinear functions. If $m > n$, then, as well as gas concentrations, the solution can include a figure of merit or confidence interval for each determined gas concentration. This is very desirable, since a personal pollution monitor will often be exposed to gases which it was not designed to measure. Even though these extraneous gases will interfere with the gas measurements, the confidence interval produced with each gas concentration will signal its validity or error.

A technique of selectivity enhancement is presently being developed for use with commercially available gas sensors. We are in the process of determining the functional dependence of device response on gases in the ambient.

TAGUCHI GAS SENSOR

Our research effort has concentrated on the testing of a variety of in-house gas sensors as well as commercially available sensors. The Taguchi Gas Sensor (TGS), which is manufactured by Figaro Manufacturing Company of Japan, typifies the state-of-the-art in gas detection. Our purpose in studying it is twofold. Its behavior is characteristic of many other metal oxide semiconductor detectors, so that knowledge of its parameters may guide research and development of new detectors. Being commercially available, it is manufactured reproducibly; we can test large numbers of them inexpensively. The other purpose of the study is the identification of parameters of the Taguchi Sensor which may be conducive to microcomputer selectivity enhancement. It may be that an already-existing detector which is used in only smoke detection may be suitable for use in gas identification.

The TGS is constructed of a highly porous, n-type, tin oxide semiconductor whose conductivity is greatly affected by the gases present at its surface. The surface reactions which determine the sensor's detection properties are strongly temperature-dependent. To control the sensor temperature, a heating coil is imbedded within the sensor. A power of 600 mw dissipated in this coil is capable of heating the TGS to about 400° C. Heating in order to achieve reasonable sensitivities to gases is a method likely to be used by most detectors we plan to test.

When heated, the Taguchi Gas Sensor is responsive to a wide variety of gases. Because of the complexity, nonlinearity, and nonspecificity of the Taguchi Gas Sensor's response to gas concentration, these devices are used only for smoke detection or explosive level indication; they are not used for low-concentration detection or gas identification.

Measurement Apparatus

A dual microcomputer data acquisition and analysis system developed by the authors is used for all measurements. It consists of three parts: a clean gas system, a dedicated microcomputer data acquisition system, and a data analysis microcomputer.

Gas System. The gas system consists of several exponential dilution bottles in which the semiconductor sensors are mounted. Gas concentrations in these bottles can be maintained accurately down to a few parts-per-million. It is possible with these systems to produce slowly changing concentrations of gases so that the data acquisition system can take data unattended over long time periods. There are several dilution bottles so that some may be dedicated to an automatic data collection system while others can be used for rapid manual testing of detectors.

Data Acquisition. A real-time data acquisition computer system measures and records the resistances of a bank of sensors mounted in the clean gas system. The data can be output in readable form to the teletype or, under program control, be transferred to the data analysis computer. The forte of this microprocessor-based data acquisition system is that it can log huge amounts of important data in an automatic, reproducible manner over long periods of time, thereby freeing the experimenter from this costly task.

Data Analysis System. The heart of the data analysis system is a SOL-20 (Processor Technology Corp.) 8080 microprocessor-based computer system. This system has a keyboard and video display for human interface. A floppy disc mass storage system gives the computer sufficient memory capability to run an interactive high-level language. The functions of the data analysis system are the following:

1) To control the microprocessor-based data acquisition system. Control parameters are passed to the data acquisition system, telling it when to take data and how to change the sensor heater voltage. The accumulated data is passed to the main computer, where it can be processed.

2) The raw data can be stored on a floppy disc, from which it can be retrieved at will.

3) An interactive high-level language (BASIC) can be used to program the data analysis functions. The data analysis will consist predominantly of curve-fitting techniques. Trial functions will be fit to the raw data, and the goodness of fit will be tested.

4) Outputs--such as best fits of curves, functional parameters, or im-

portant intermediate results--can be delivered to either a teletype or video display.

Experiments. Data acquisition and analysis experiments are of two broad classes: investigation of the steady state response of the detectors to ambient gas concentrations; and determination of the dynamic response of the sensors to a step change in gas concentration or temperature. Most experiments are done automatically by the computer system so that they may be reliably repeated at a later time or for other conditions.

Results

Steady State Response. When TGS sensors operating at 5-V heater voltage are placed in pure N_2, their resistances drop from "air" values of approximately 10 to 20 KΩ to very low values (.5 to 2 KΩ). In addition, the sensors' resistances are observed to drift over a large range (of up to a factor of 2) over time periods of hours to days in a constant environment. If O_2 is added, the resistances increase--nearly following a power-law relationship--until in pure O_2 they are the greatest observed (500 KΩ to Ωm). Figure 1 shows this power-law response for several sensors. Resistances of individual sensors start at vastly different values, but all show similar power-law slopes.

If one starts with a high O_2 concentration (for instance, pure O_2 or air) and adds either H_2, CH_4, wet CO, or H_2O, very similar curves are produced (as shown in Figure 2). The resistance versus concentration is again described by essentially a power law, but now the resistance decreases. The remarkable feature of these curves is that their slope is the negative of the slope of increasing resistance in O_2 concentrations.

An equation which fits these curves very well is found to have the following form

$$R = (K_o + K[C])^{-\beta}$$

for H_2, CH_4, CO, H_2O; and for O_2, replace $-\beta$ by $+\beta$.

Where R = resistance of sensor
K_o = a detector dependent constant which describes the finite resistance at zero gas concentration

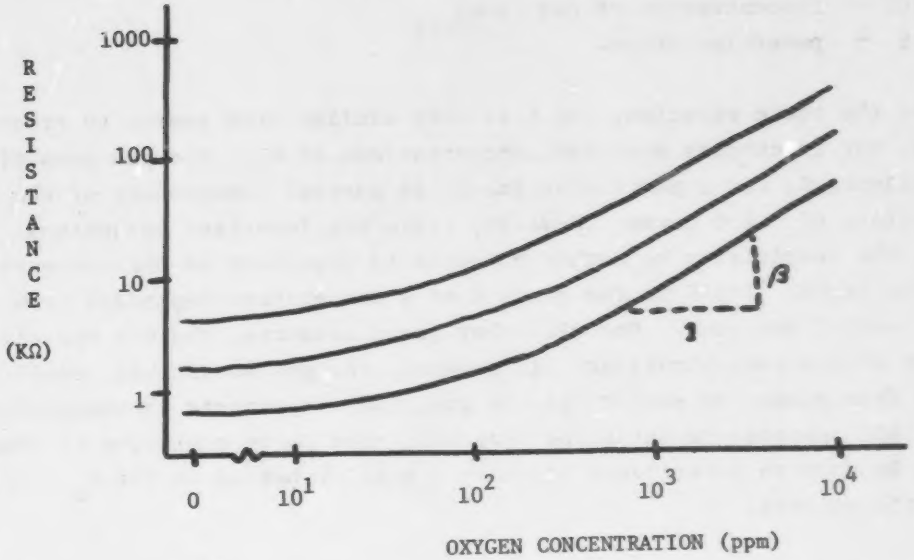

FIGURE 1. TGS resistance versus oxygen concentration in nitrogen. The response approaches a power law for high concentrations. $R \sim K[O_2]^{+\beta}$ where β is the power-law exponent.

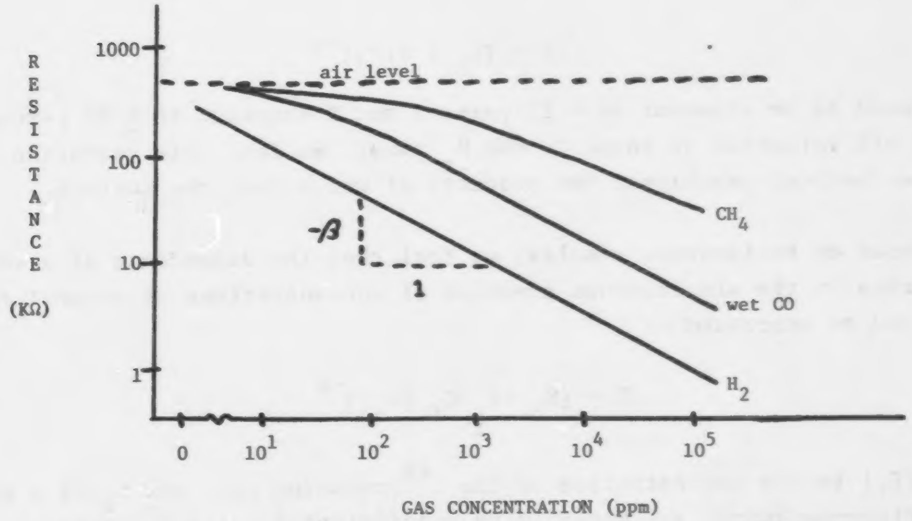

FIGURE 2. TGS resistance versus reducing gas concentrations in an air ambient. For high concentrations, the response is power law: $R \sim K_1[C_1]^{-\beta}$. Differing gas sensitivities, K's, are evident in the separation of the curves.

K = a constant which is specific
to a sensor and the type of gas
[C] = concentration of gas (ppm)
β = power-law slope.

In the above equation, the β is very similar from sensor to sensor or gas to gas, but it changes sign for concentrations of O_2. The gas sensitivity coefficient, K, for a particular gas is in general independent of the concentrations of other gases. However, there are important exceptions. In particular, the sensitivity to carbon monoxide is dependent on the concentration of water vapor. Its K is the product of a temperature-dependent term and the water partial pressure. For all other gases measured, the K's are all independent of gas concentrations. In general, the gas sensitivity coefficients change from sensor to sensor, gas to gas, and temperature to temperature. It is this temperature variation that will need to be exploited if these sensors are to be used to selectively identify a gas. Imbedded in the K_o term are the drift effects.

For a single sensor operating at constant temperature, there is a day-to-day variation in resistance, even in a very "clean" atmosphere. If the dependence of sensor resistance on CH_4 concentration in air is measured on different such days, a family of curves is obtained, each with a different starting point but with other essential features much the same. If these curves are optimally fit to

$$R = (K_o + K[C])^{-\beta}$$

β is found to be constant to ± 25 percent and K constant to ± 10 percent. Almost all variation is found in the K_o term. We feel this variation is due to slow chemical reactions, the products of which foul the surface.

Based on preliminary results, we feel that the dependence of a sensor resistance on the simultaneous presence of concentrations of several reducing gases can be expressed by

$$R = (K_o + \Sigma_i K_i [C_i])^{-\beta}$$

where $[C_i]$ is the concentration of the i^{th} reducing gas, and K_i is a strongly temperature-dependent gas sensitivity coefficient for the i^{th} gas.

This expression suggests that if there is enough temperature variation among the sensitivity coefficients K_i, then it may be possible to produce gas specificity by varying the temperature. Long stabilization times and hysteresis effects greatly complicate data collection when the temperature is varied. If, however, at different temperatures the resistance versus concentration characteristic is measured, and then the corresponding relationship between resistance and temperature at constant concentrations is obtained, then a graph similar to that shown in Figure 3 would be obtained. Here, we can see that temperature dramatically affects the zero-concentration resistance as well as the sensitivity to the gas. If such curves for different gases show different sensitivity functions versus temperature, then, conceptually at least, we have a means of improving the specificity of the sensors to various gases.

The dependences of the sensitivity coefficients on temperatures have not as yet been well determined for any gas other than methane. Preliminary data suggest, however, that they are characteristically different functions, as shown in Figure 4. Experimental effort is continuing to characterize these functions further.

Transient Response. When the temperature of a Taguchi Gas Sensor is abruptly changed, its resistance exhibits a very complex transient response, as shown in Figure 5. There is a sudden peak (or dip, depending on the direction of temperature change) and a slow relaxation towards the initial value. This is followed by a very slow drift in resistance extending from 10 minutes to 3 hours. The sudden peak and its relaxation can be understood in relation to the chemisorption processes occurring at the surface of the material. Other metal oxide semiconductors show very similar behaviors. The very slow change occurs as the material reaches a new equilibrium with the oxygen ambient. This interpretation is confirmed by studies using Auger Elemental Analysis, which show changes in the oxygen content and stochiometry of the tin oxide material with changes in temperature. Measurement of the transient response for many step changes of temperature in the 400° to 800° K range, and subsequent analysis of the time constants observed, are yielding valuable insight into the evolution of chemisorptive models for device behavior.

TGS Selectivity Enhancement

The general response of a Taguchi Gas Sensor to the reducing gases H_2, CH_4, and CO is:

$$R = (K_o + K_1[H_2] + K_2[CH_4] + K_3[CO])^{-\beta}$$

FIGURE 3

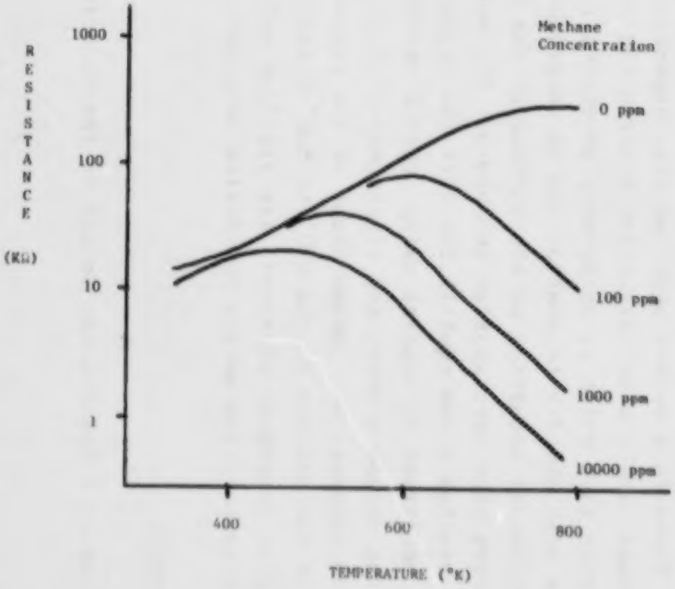

FIGURE 4

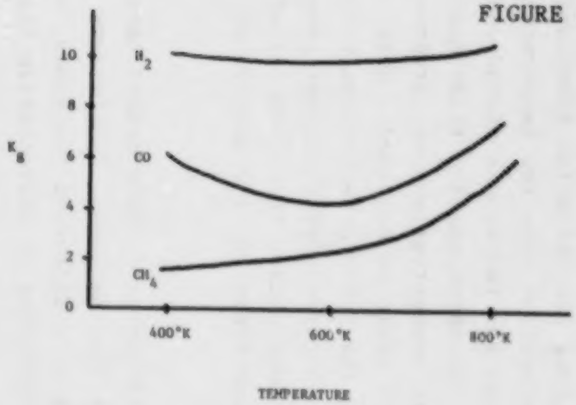

FIGURE 5

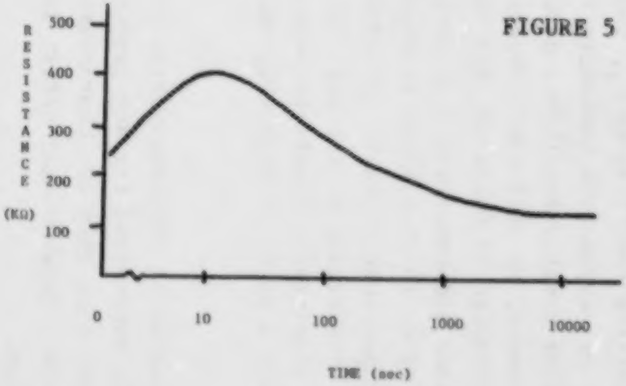

FIGURE 3. Detector resistance versus temperature in various concentrations of methane in air. The detector's sensitivity steadily increases with increasing temperature. FIGURE 4. Variation of gas sensitivity coefficients with temperature (not to scale). The sensitivity to each gas is a characteristic function of temperature. FIGURE 5. Transient response of the TGS to a step change of temperature. The initial peak and relaxation reflects a change in chemisorptive equilibrium at the semiconductor surface. The subsequent slow drift, due to chemical and stochiometric change, may persist for several hours.

Because the K's are strongly temperature-dependent, the response may be measured at several temperatures and the system of equations solved numerically for the gas concentrations. A complication arises with the gas CO. Sensitivity to it depends on water concentration; an independent measurement of water vapor pressure may be necessary. It is possible that in an atmospheric ambient of normal relative humidity, the error introduced by ignoring the dependence on water vapor will be negligible. Measurement of the gas sensitivity coefficients will reveal whether this is the case.

Another important complication is the long stabilization time introduced by an abrupt change in temperature. This prevents the measurement of response by sequentially changing the temperature. We are rapidly gaining knowledge of the causes of long stabilization times and expect to be able to computationally extrapolate stable values from initial transients. This will enable the manipulation of temperature in real time, producing detection times suitable for personal dosimetry. An alternative would be to use several sensors, each of which operates at a different temperature. Because the temperature of each is constant, the detector's behavior is stable. The only disadvantage to using several sensors is the power consumption needed to maintain the high temperatures of the devices--about one-half watt each.

Of course, filters may be cascaded around several Taguchi Gas Sensors, expanding the above response equation into a system of independent equations. The filters need not select perfectly for and against specific gases; they need only produce sufficiently different, effective sensitivity coefficients for a computer solution to be possible. A disadvantage of this solution is the bulkiness of the sensors and filters and the resulting power consumption. On the development front, we expect the integration of several sensors and filters on one chip, obviating many of these difficulties.

CONCLUSION

Materials research will continue to alter the catalytic activity of semiconductor surfaces so that solid state gas detectors will become more selective. But, at the same time, pollution research monitoring needs are evolving from the measurement of hazardous levels of a few simple gases to the determination of less than a part per million of many highly complex organic vapors. To keep up with these needs, we will not only need more sensitive and selective sensors, but also increased intelligence in the measurement instrument.

The newly developed microprocessor technology can meet this need.

Microcomputers of sufficient capability and small enough size for personal dosimetry are now being marketed as hand-held data-entry terminals for inventory control and costing (due to their massive memory and market considerations) at about $900. This cost could easily drop, for a mass-produced instrument, to the $30 range. Fully programable scientific calculators are now available for under $30. The projected downward cost of microprocessors and their peripherals should make the microprocessor-based system increasingly attractive for personal monitor applications.

We have shown that, at constant temperature in an oxygen-rich ambient, the TGS resistance, R, varies with reducing gas concentration [C] as $R\ K[C]^{-}$, where K is a sensitivity coefficient peculiar to the reducing gas and the operating temperature, and is a power-law exponent. It seems possible that the dependence of the sensitivity constants K for various gases on detector temperature can be utilized to enhance the TGS selectivity in gas detection. The major complication to this scheme would be the long stabilization times involved when temperature is changed. Nevertheless, a synergistic combination of semiconductor sensors and microcomputer-based signal processing is expected to help overcome the most significant limitation of present sensors--their lack of selectivity.

ACKNOWLEDGEMENT

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Discussion

(NOTE: The following discussion took place after the presentation of the papers "Studies of Semiconducting Metal Oxides in Conjunction with Silicon for Solid State Gas Sensors" and "Microcomputer Control and Information Processing Technology for Semiconductor Gas Sensors.")

SHAW: Bob Shaw from EPA. I would expect that water vapor would be tenaciously absorbed on these surfaces--much more strongly absorbed than the molecules that are of interest. And since there can be several percent of water vapor in a typical atmospheric sample, the water vapor could very likely be taking up most of the sites on the surface. Would you have to dry the samples?

CLIFFORD: Most of the metal oxides' detectors were achieving the detection efficiency at very high temperatures. At very high temperatures, there is not much of anything really adsorbed sitting on the material at one time, so that the surface coverage is much less than a monolayer for water and all of the other gases of interest.

Now, we may have trouble with a lot of water sitting on the material condensed, as well as maybe some other gases at the lower temperatures. So far we have been operating at high temperatures, and it is not a problem.

There is a sensitivity to water just as there is a sensitivity to other reducing gases.

SHAW: I guess I missed hearing about the mechanism of operation. It seems to me that if water vapor is more strongly adsorbed than many of these other gases--and yet if it is the modulation of the adsorbed oxygen that gives you the change in resistivity--I just don't see how raising the temperature will correct this?

JORDAN: Of course. We operated at temperatures on the order of 200°, 300°, 400° Centigrade.

SHAW: But then all these other gases will be desorbed way below those temperatures?

CLIFFORD: They are desorbed at specific temperatures. The surface of the material is very heterogeneous. There are adsorption activation energies that cover a wide spectrum of energy, so that in any given temperature range a great many gases are adsorbed in different ways and at different activation energies.

SHAW: What I should have asked, I suppose, is have you seen that relative humidity does not affect the behavior of your detector surfaces?

JORDAN: Of some temperatures, more; of some temperatures, less. Three hundred or 400° Centigrade temperature is the range for the device with which I am working. The effect is not deleterious.

CLIFFORD: Also, water vapor is actually detected by the sensor.

JORDAN: It is another component of the mixture which you have to reckon with.

BURTON: Bob Burton, EPA. What is the probability of getting your sensitivity down by a factor of 10?

JORDAN: The ppb's rather than ppm's?

BURTON: Yes.

JORDAN: It is fair to say that at the moment our lead oxide, tin oxide for leading devices, was in ppm's. I think you can go to lower. I think it would be coupled under there.

SCHEIDE: Gene Scheide. One of your original advantages was to use a single broad purpose sensor to sense many gases. But in the end, are you saying that you have to use one sensor for each gas operating under a different condition?

CLIFFORD: We won't need one sensor for each gas. What we need are a couple of independent sources of information. That can be three or four sensors or one sensor operated at three or four temperatures.

SCHEIDE: You need a different sensor operating on a parameter for each gas?

CLIFFORD: For each gas; that is right.

SCHEIDE: Do the number of variables have any relation as to the equal number of gases being analyzed?

CLIFFORD: Yes; we need at least that many degrees of freedom or more for independent methods. The advantage of deconvolving this information through the computer is also that when we have more sources of information, we determine, as well as the gas concentration, the degree of validity of that concentration--an error down the line for every gas measured.

JORDAN: But remember this is not going to be coupled. But they are beginning to be coupled already to the silicon chip.

CLIFFORD: So, we can see one sensor that eventually has mounted on it 12 different filtering arrangements or 12 different sensors. But by being swept in temperature, it gives us essentially 100 temperatures now.

SCHEIDE: But another one of the problems was temperature stability--correct?

CLIFFORD: Yes. Right now there are metallurgical problems with that. Also, we don't really know a lot about the temperature reactions. It may be that once we know a little bit more about them, that just by looking at the initial transient when the temperature is changed, we can predict what the stable value would be an hour later.

Management Strategy in the Design and Use of Personal Monitors for Environmental Studies

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It is not difficult to develop justification and enthusiasm for the development and application of personal monitors for advanced epidemiological studies on environmental pollution problems. Indeed, by this time most of the participants at this symposium are probably at a fever pitch in their realization of the importance of the whole thing. In a situation like this, it would be all too easy for us to go screaming off in all directions, wasting an enormous amount of time and effort and requiring us to come back later and do the careful preprogram planning that we should do at this time. This is a plea for careful attention to such planning at the management level.

To begin with, what we are proposing to do is to develop a system for measuring and recording a variety of parameters (exposure and health effects) that are not easy to measure accurately, even under carefully controlled laboratory conditions. We proposed to design these measuring and recording devices into a single package, small enough to accompany an individual human throughout his or her entire day's activities, cheap enough so that we can afford to place thousands of these in the field, yet powerful enough so that we can be thoroughly confident that the measurements made with the system are of such quality and validity that they can be defended against the most vigorous attack.

One of the most important factors in this development is that when these personal monitoring devices are placed in the field, they must be of one single design for any one complete study. It may be that we will eventually end up with several devices from which we can choose one to be used in a particular study; a little later on, I will espouse the value of the development of a modular system that can be adapted to a particular study. In any case, we cannot depend on haphazardly dissociated competitive development for this particular task.

To be sure, the individual devices or components will surely be developed by various agencies--governmental, university, and private industry. But in the long run, these individual components must be assembled into a personal monitor within a single, well-defined program unit. An agreed-upon set of Quality Assurance criteria must be met, and there must be a carefully designed and implemented performance testing program. Therefore, the planning phase of the entire development program is at least as important as the actual development. This planning is the responsibility of management, and management must be made aware of this responsibility at the outset of the program.

I suspect that almost all of us here are aware that the program we are discussing is no small effort. Indeed, when one carefully considers the requirements of the ultimate development and compares these with the state-of-the-art in the several fields of instrumentation involved, the whole affair becomes a little frightening. My thesis is that we must somehow manage to impart this appreciation of the magnitude of the task facing us and the difficulties involved to the management components of every agency to be involved. Only with the intelligent and enthusiastic participation of management can the program be mounted at all.

All of us who work daily with the generation and measurement of air pollutants and air pollutant mixtures are constantly aware that accurate measurement of those pollutants is a continuing problem, even in the fixed-laboratory situation. The amount of time and effort spent in checking, calibrating, and adjusting the measurement instruments is large. Now we are proposing to develop a system which will measure and record those values without constant attendance over a considerable period of time, and which will be small enough and portable enough so that it can accompany the individual human subject as he or she moves around in his or her normal daily routine.

The state-of-the-art in pollutant measuring devices can only be described as being in the early developmental phase. To be sure, there are a number of devices in existence which give promise of being useful for personal monitor development. When these devices are finally evaluated for use under the conditions I have described, some of them will in fact prove to be useful, and others will not. I am virtually certain that some measurement components will have to be developed almost from scratch.

We remember, of course, that the personal monitor is intended for the continuous measurement of not only the air pollutant levels, but also those health effect parameters that are indicative of deleterious effects of the pollutants. And if we are completely honest about it, we have to admit that we may face more difficulty in this phase of the development than in the pollutant-measurement phase. The physiological parameters that are easy to measure--the ECG, body temperature, respiratory movements, and so on--are unfortunately not useful as indicators of health effects decrements produced by ambient levels of air pollutants.

In fact, the physiological variables which are indicative of pollutant effects are very difficult to measure with the accuracy required, even in the laboratory environment. Let us examine just a few of these to support this statement.

It is well established that the most detectable physiological changes associated with exposure to most pollutants are changes in lung mechanics, and that most significant among these is the resistance of the airways. This effect of pollutants on airway resistance is especially important in people who are already suffering from pulmonary disease--asthmatics, people with emphysema, people with black lung disease, byssinosis, silicosis, and so on. Unfortunately, the measurement of airway resistance is a relatively difficult process, especially under the conditions under which the personal monitors are expected to be used.

There are two ways of approaching the airway resistance problem. One of these is direct measurement, and the other is derived measurement from the analysis of air flows in special respiratory maneuvers. For field epidemiological studies, the direct measurement of airway resistance is hopeless at the present state-of-the-art. There are only two commonly accepted methods for this; one is the use of a body plethysmograph, which by no stretch of the imagination could be made into a personal monitoring device. The other requires the measurement of the intraesophageal (representing intrathoracic) pressure, and this involves the subject having an intraesophageal balloon in place. It is inconceivable that general population subjects could be induced to have such a balloon introduced and left in for the required length of time. Therefore, unless someone comes up with an entirely new technique for direct measurement of airway resistance, we can forget that approach. I will not say we are completely dead in this area. It is barely possible that the relatively noninvasive but not thoroughly proven forced oscillation technique might be developed to the point that it could become useful in personal monitoring. In its present condition, this would not be true.

The indirect measurement gives more promise for personal monitor use. This indirect measurement is actually a measurement of the maximum rate at which the subject can expel air from the lungs. This maximum flow rate can be measured with a device called a pneumotachometer, which can conceivably be developed into an instrument that could be clipped or pinned to the subject and used only at intervals. My conception of the ultimate form of this pneumotachometer is shown in Figure 1. Its output is electrical, and thus is amenable to recording and/or analysis in portable monitoring equipment.

The use of this pneumotachometer unfortunately requires that the subject perform a very special kind of respiratory maneuver. He or she must expel the air from the lungs at a maximal rate. In the laboratory, he is coached into putting all his effort into the air expulsion, and even with such coaching, the maneuver is not always successful. For field use, the subject would have to be carefully trained to perform the maneuver in the right way, and would somehow have to be programed so that he would make a maximal effort at every measurement time. There would be no attendant coaching him or observing his performance. If he does not perform quite to the maximum, the indicated maximum air flow is reduced, and this sort of reduction is exactly what we would be looking for if a pollutant effect were experienced. Therefore, it is going to be very difficult to tell whether an apparent decrement in air-flow capability is due to a pollutant effect or to a failure on the part of the subject to exert maximal effort. It is obvious that even in this relatively simple sort of measurement, its adaptation to personal monitoring is highly questionable.

What else can be measured that might give some indication of deleterious effects of air pollution? Not much. We have reason to believe that some pollutants have effects on the body's immune systems, but these cannot be measured in the personal monitoring situation. Some of them may (and probably some do) have carcinogenic effects, but these cannot be measured in personal monitoring. It is possible that air pollutants may affect cardiac performance in those individuals (cardiac patients) who do not have a reserve on which they can call in pollution-stress situations. Therefore, the ECG probably should be measured and/or recorded. Unfortunately, ECG interpretation is not amenable for use in the personal monitoring situation; it still depends almost entirely on the use of pattern recognition by trained humans. There are, of course, computer programs that can be adapted to this analysis, and I am sure that these could be developed to make ECG analysis more feasible for personal monitoring purposes.

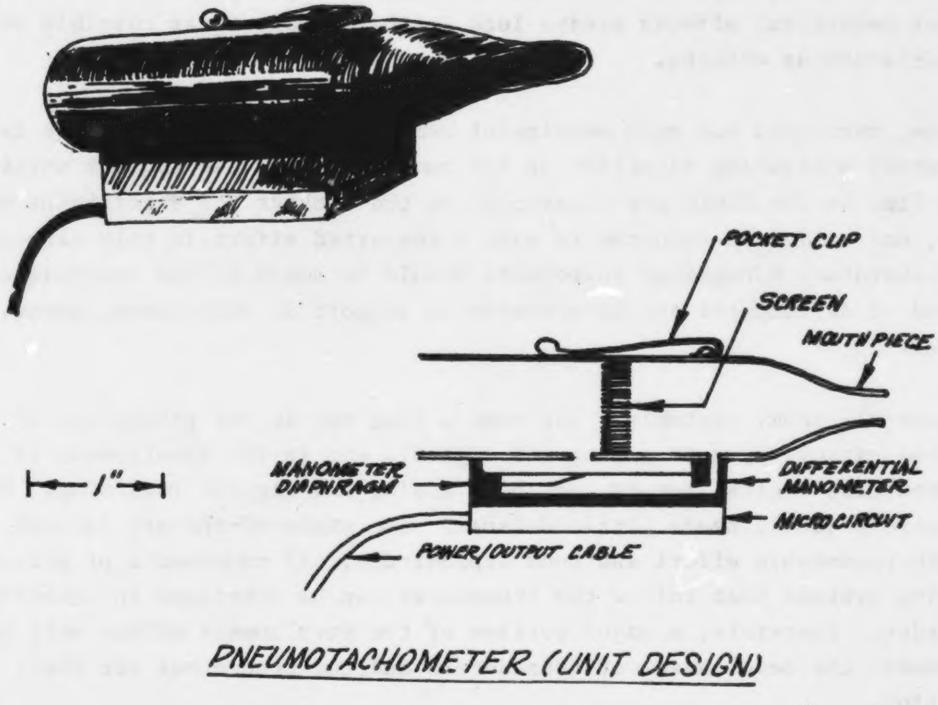
POCKET CLIP
SCREEN
MOUTH PIECE
MANOMETER DIAPHRAGM
DIFFERENTIAL MANOMETER
MICROCIRCUIT
POWER/OUTPUT CABLE
1"
PNEUMOTACHOMETER (UNIT DESIGN)

FIGURE 1. Diagram and sketch of one way to design a transducer for use in a personal monitoring system. Currently used pneumotachometers have the pneumotach tube and screen, the differential pressure manometer, and the basic circuitry as separate components, and are very large and cumbersome.

There are some fairly interesting developments occurring in electrical impedance plethysmography which could be of value in personal monitoring. This field, and the techniques associated with it, would have to be explored thoroughly. I am sure this would provide a way for continuous recording of general respiratory movements, so that we could monitor coughing frequency, etc. In general, electrical impedance-measured parameters are at best only semiquantitative.

The measurement of body temperature is well within the state-of-the-art, but is of doubtful utility in personal monitoring for air pollution health effects. It might help us to detect those individuals who have an infection, and there is always an outside chance that ambient levels of some as yet unknown pollutant may have a body temperature effect. I doubt that it would cost us much money or effort to include this measurement capability.

One other possibility is the development of some measure of mental alertness, responsivity, etc. Certainly some attention should be paid to this, for behavioral effects always lurk in the background as possible pollutant deleterious effects.

Thus, there are not many meaningful measurements that can be made in the personal monitoring situation on the human himself. We who are working all the time in the field are constantly on the lookout for significant measurables, and we may be required to make a concerted effort in this direction. Again, laboratory management components should be aware of the importance of this kind of development and be prepared to support it with funds, space, and personnel.

As we all know, technology has come a long way in the production of integrated circuitry, both analog and digital, and in the development of microcomputers, digital memory, and both analog and digital recording. My next thesis probably needs little defense: the state-of-the-art is such that with reasonable effort and fund expenditure, all components of personal monitoring systems that follow the transducer can be developed in relatively short order. Therefore, a major portion of the development effort will have to be toward the development of transducers and the procedures for their application.

My own conception of the personal monitor is of one utilizing full modularity. With chip design and production as it now exists, it should be possible to design and produce a series of integrated circuits, including amplifiers, signal modifiers, A-D converters, telemetering circuits, counting circuits, smoothing and differentiating circuits, and so on down the line. These would be designed to be incorporated into a packaging unit having pins on the bottom and sockets on the top, so that they could be stacked to produce any combination of circuits desired. One row of such connections would carry through the entire stack, providing power from the bottom or base unit to all the circuits in the assembly; another row would effectively serve as a signal bus, carrying analog or digital signals as required. All package modules would be identical and could be assembled in any combination desired. I visualize these as being approximately 1 inch X 2 inches X 1/4 inch.

Power modules would necessarily be larger than the circuit modules. Thus, I have generally considered these as being the bottom units. The power modules could be snapped together horizontally, so that several different monitors could be incorporated into a single package. This general scheme is visualized in Figure 2.

I have also considered that there will probably need to be two types of terminal (top) units. One of these would be capable of recording or storing in digital form the data derived throughout the period of monitoring. This will become more and more in the realm of possibility as promising new developments in storage memory come to fruition, and when it becomes possible to store millions of bits of information in a couple of cubic inches of space. This type of storage would be limited to relatively small data productions, for even if it is decided to accept 8-bit digital data, the number of data words that can be stored has a quite finite limit. This concept is illustrated in Figure 3.

The other possibility (and I suspect this will emerge as the most important possibility) is the telemetering of information from the unit worn on the person to a receiver/computer/recorder combination housed separately in a briefcase-type of enclosure that could be set anywhere within a few hundred feet of the monitored individual. This unit would only need to be moved if the individual himself moved beyond the range of the telemetering device. This unit could also be the source of an alarm signal which would alert the individual to the fact that it was time to perform a required respiratory maneuver, etc. This unit might also include a voice tape recorder on which the subject could note any special activities he engaged in--again, by telemetering to the recording unit.

Thus, those of us in clinical research do have a major interest in personal monitoring, and we have some ideas for the design of such monitors which we think may be of value. At this time, we are pursuing these ideas at a low level, and we hope to increase our effort in the near future.

Ultimately, it is likely that the greatest contribution the Clinical Studies Division of EPA can make to the personal monitoring development program may be in the Quality Assurance procedures which will be required before the monitors can be accepted for field use. Not only will it be necessary

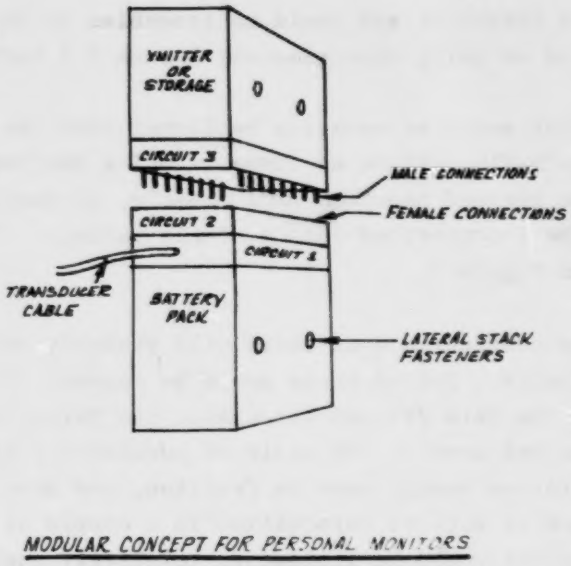
XMITTER OR STORAGE
CIRCUIT 3
MALE CONNECTIONS
FEMALE CONNECTIONS
CIRCUIT 2
CIRCUIT 1
TRANSDUCER CABLE
BATTERY PACK
LATERAL STACK FASTENERS
MODULAR CONCEPT FOR PERSONAL MONITORS

FIGURE 2. Conception of a modular system for design of personal monitors. Each monitor assembly would serve for monitoring one parameter. Multiple parameter monitors would consist of several of these fastened together side-by-side.

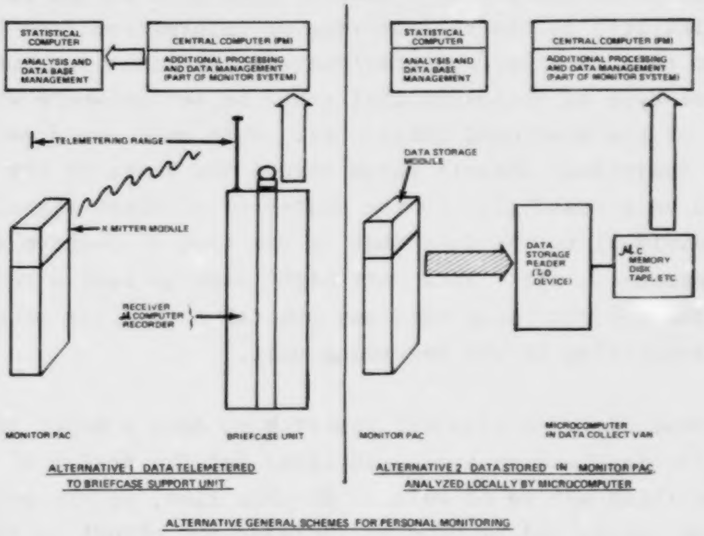
STATISTICAL COMPUTER
ANALYSIS AND DATA BASE MANAGEMENT
CENTRAL COMPUTER (PM)
ADDITIONAL PROCESSING AND DATA MANAGEMENT (PART OF MONITOR SYSTEM)
TELEMETERING RANGE
X MITTER MODULE
RECEIVER
μ COMPUTER
RECORDER
MONITOR PAC
BRIEFCASE UNIT
ALTERNATIVE 1 DATA TELEMETERED TO BRIEFCASE SUPPORT UNIT
STATISTICAL COMPUTER
ANALYSIS AND DATA BASE MANAGEMENT
CENTRAL COMPUTER (PM)
ADDITIONAL PROCESSING AND DATA MANAGEMENT (PART OF MONITOR SYSTEM)
DATA STORAGE MODULE
DATA STORAGE READER (I-O DEVICE)
μC MEMORY DISK TAPE, ETC
MONITOR PAC
MICROCOMPUTER IN DATA COLLECT VAN
ALTERNATIVE 2 DATA STORED IN MONITOR PAC ANALYZED LOCALLY BY MICROCOMPUTER
ALTERNATIVE GENERAL SCHEMES FOR PERSONAL MONITORING

FIGURE 3. Two possible ways of handling the problem of data storage and/or recording in the personal monitoring situation. In Alternative 1, the subject would "wear" the transmitting monitor, but recording would be carried out in a larger, heavier but still portable briefcase-size package. In Alternative 2, which depends on not-yet-available digital storage capacity, the data are stored in the monitor itself.

to show that the individual monitors can measure air pollutants or health effects parameters with acceptable accuracy and dependability, but it will also be necessary to show that the monitors can be worn by the subject all day long without causing him or her undue discomfort or without restricting his/her movements. The monitors must be tested with all components (environmental and health) operating in a situation where actual changes in pollutant levels are occurring. This kind of testing--the final step in certification of quality assurance--can only be carried out in exposure chambers of the type that we have.

In the final analysis, only the clinical scientist can make the most important judgment of all--whether observed alterations in the monitored health variables can be considered to be indicators of decrements in human health. That is what the whole program is about. The Clinical Studies Division of EPA wants and expects to play a significant role in the personal monitor development program, as well as in the ultimate program of use of the monitors.

The personal monitor development program will surely involve the efforts of many individuals from many different fields. If any major effort were ever multidisciplinary, this one is. Management components of the agencies involved, whether they are government laboratories, university laboratories, private research organizations, or industrial groups, must be aware of the total requirements of the program, and must be made to recognize that a new and unique type of effort is required in this program. There must be a degree of organization of the effort which has not been put together up to this time, and this will require new management techniques.

Without complete management involvement and collaboration in this developmental effort, the tasks will be much more difficult. On short notice, there must occur some major reprograming of funding and staff assignments. I believe that each of us must carry this message to our management, and those of us in management must launch a major search for ways and means of accomplishing the important job needed for the development of personal environmental and health monitoring systems.

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The Usage of Personal Monitors for Determination of Dosage and Exposure in Health Effect Studies

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INTRODUCTION

The health effects of a pollutant are a function of the amount of the material absorbed by the human protoplasm through exchange processes in the lungs, the digestive system, the skin, and other organs. For the gaseous pollutants such as carbon monoxide (CO) and ozone (O_3), the health effects are primarily produced from exchange processes in the lungs, although eye irritation may be caused by absorption directly into the eye. For ozone, eye irritation and lachrymation may be dependent on the exposure to concentration of O_3 at the eyeball surface. However, for lung irritation and respiratory effects, the health effect may be dependent upon dosage of material absorbed into the protoplasm at the gas exchange interface. In design of epidemiological studies to test hypotheses of health effects produced by pollution, it is important for us to consider both dosage and exposure as variables upon which the health effect is dependent.

The following sections describe the technical considerations for studies to assess exposure and dosage and the application of personal monitors in these studies.

EXPOSURE ASSESSMENT AND RELATION TO HEALTH

A health effect of oxidants such as ozone and peroxyacetylnitrate (PAN) is eye irritation. We may hypothesize that the severity of the effect during the study period is a function of the number of oxidant molecules which are absorbed into the eye fluids per unit time. The rate of mass transfer from the ambient air into the eye fluid may be modeled as a function of the ambient concentration and the physical properties of the fluids such as solubilities, diffusion coefficients, etc. Because these physical properties are relatively constant for exposed individuals, the only necessary variable to be measured is the ambient concentration. The chemical properties of the eye fluids will vary between individuals and cause different responses to a constant exposure. In this case, the dosage to the eye is directly dependent upon the ambient concentration, and a correlation can be made between the measured health effects and the exposure.

During an epidemiological study, a person is exposed to air pollution in many different ways. For simplicity, four exposure categories may be defined as follows:

1) Ambient (outside buildings)
2) Residential (indoors at home)
3) Occupational (at work, indoors, or out-of-doors)
4) Miscellaneous (in a vehicle, at a theater, etc.).

The average exposure $\bar{X}_E$, in the period T, can be represented by Equation 1.

$$\bar{X}_E = \frac{1}{T} \int^T X dt \qquad [1]$$

where X represents the concentration to which the person is exposed in each of the four categories described above during the study period T.

Assuming a control is available for the experiment by a measured response to low-level exposures, $\bar{X}_E = 0$, the excess health effect can be defined $\Delta HE = f(\bar{X}_E) - f(0)$. The excess health effect ΔHE can be plotted versus $\bar{X}_E$ and a correlation developed. Figure 1 shows the expected results from an experiment in which the underlying relationship is linear. The data points will scatter about the regression line, and the correlation coefficient will be close to 1. These results are obtainable if the exposures of all the experimental subjects are computed by Equation 1. In practice, however, this may not be possible. Several epidemiological studies have compared the excess health effects observed in the study populations, ΔHE, with the average ambient or outside air concentration of the pollutant, $\bar{X}_1$. If we were able to measure $\bar{X}_E$ for all study subjects, the distribution of the integrated exposures would have a finite variance, and $\bar{X}_1$ may or may not be close to the average exposure concentration of the n subjects in the health study

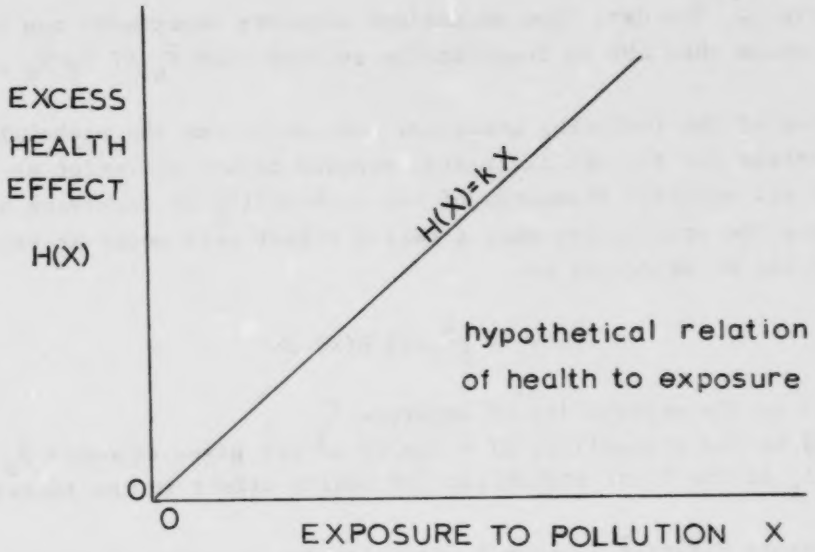

FIGURE 1. Linear relation of excess health effect to pollution exposure.

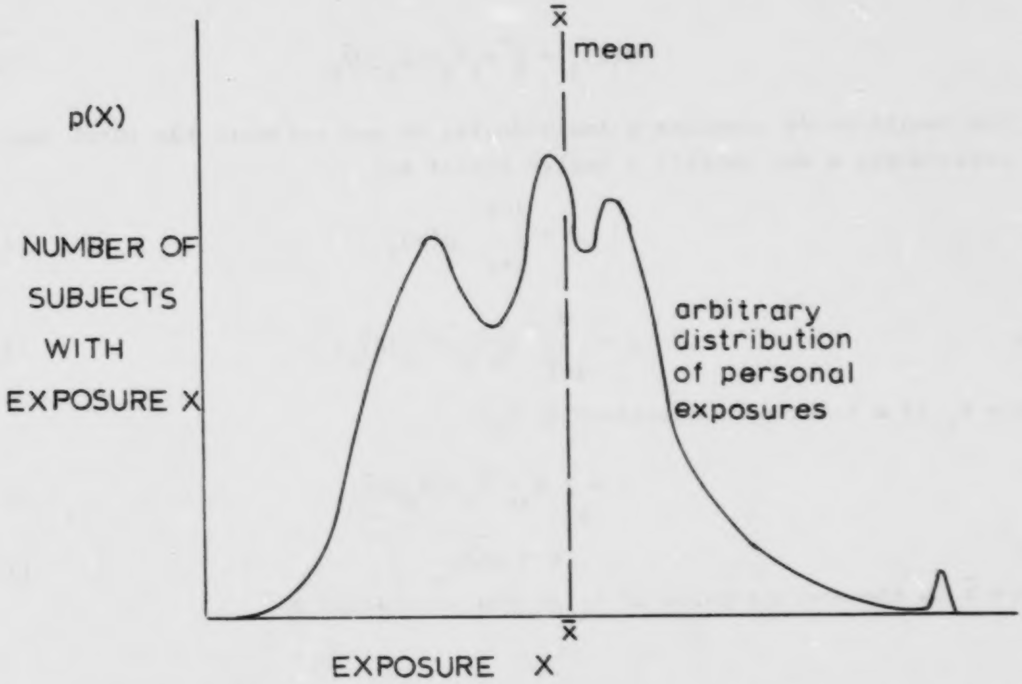

FIGURE 2. Hypothetical frequency distribution of population exposure to pollution.

defined as $\bar{X}_{E_n}$ where $\bar{X}_{E_n} = \sum_{j=1}^{n} \bar{X}_{E_j}/n$. A distributional relationship may be as shown in Figure 2. The data from an ambient exposure experiment can lead to a valid conclusion when ΔHE is functionally related with $\bar{X}_E$ if $\bar{X}_I = \bar{X}_{E_n}$. This is demonstrated by the following analysis. We can define the probability of a health effect for the ith individual exposed to air pollution as the integral over all possible exposures of the probability of receiving an exposure, X_E, times the probability that a health effect will occur at exposure X_E. This relation can be expressed as:

$$p(H)_i = \int_0^\infty p(X)\, H(X)\, dX \qquad [2]$$

where: p(X) is the probability of exposure $\bar{X}_E$
H(X) is the probability of a health effect given exposure $\bar{X}_E$
$p(H)_i$ is the total probability of health effect in the individual i.

Let us assume $H(X)=k_i\bar{X}_E$, where k_i is a complex function of other variables such as age, sex, race, smoking habits, physiological state, and past exposures to pollution of the ith individual. Substitution into Equation 2 gives:

$$p(H)_i = \int_0^\infty k_i\bar{X}_E p(\bar{X}_E) d\bar{X}_E \qquad [3]$$

If the health study examines n individuals, we may estimate the total number of individuals m who exhibit a health effect as:

$$m = \sum_{i=1}^{i=n} p(H)_i \qquad [4]$$

and

$$m = \sum_{i=1}^{n} \int_0^\infty k_i\bar{X}_E p(\bar{X}_E) d\bar{X}_E. \qquad [5]$$

Since k_i is a function independent of $\bar{X}_E$:

$$m = \sum_{i=1}^{n} k_i \int_0^\infty \bar{X}_E p(\bar{X}_E) d\bar{X}_E \qquad [6]$$

and

$$m = n\bar{k}\bar{X}_{E_n} \qquad [7]$$

where $\bar{k}$ is the average value of k_i in the population n.

If the average ambient air concentration, $\bar{X}_1$, is approximately equal to the mean value $\bar{X}_{E_n}$, $(\bar{X}_1 = \bar{X}_{E_n})$, then the experiment can lead to a valid relationship between health effects and measured exposures. In the case where $\bar{X}_{E_n} \neq \bar{X}_1$, the relationship will either underestimate or overestimate the effect of the pollutant on human health unless there is a known consistent relation between $\bar{X}_1$ and $\bar{X}_{E_n}$.

EXPERIMENTAL DESIGN

The design of an experiment to relate population exposure to health effects requires knowledge of both the average value of k ($\bar{k}$) and the average value of $X_E(\bar{X}_{E_n})$. The value of $\bar{k}$ can be determined from clinical evaluations and knowledge of the age-health relations of the population. The value of $\bar{X}_{E_n}$ requires measurement of the distribution of $\bar{X}_E$. One method for estimating the mean exposure of the community is to use the technique of random sampling (1). An outline of a study design contains the following elements:

1) Estimation of the variance of the exposure distribution. A pilot study of selected individuals may give estimates of the minimum and maximum exposures as well as the variance (σ^2) of the distribution.

2) Detailed Study Design. Based upon the estimate of the variance, a detailed sampling design can be made to achieve an estimate of the true mean exposure with any combination of accuracy and confidence level desired. The constraints of time, cost, logistics, etc., are all considered, and the number of individuals to be sampled is chosen. The result is a study designed to measure the mean population exposure within ΔX ppm at a γ percent level of confidence. In general, the measured mean of a set of n random samples, in the limit as n becomes very large (∞), is a member of a normally distributed population with mean $\bar{X}_{E_n}$ and variance σ^2/n. For small n, the Student's t-distribution is required to set the levels of confidence. For example, if we estimate the variance of the distribution of exposures as 16 ppm^2 and we take 36 random samples, the mean of the 36 samples will be within $\left(2.03\sqrt{\frac{16\text{ppm}^2}{36}}\right)$ 1.35 ppm of the true mean, 95 percent of the time.

3) Conduct the experiment. Sample the exposures of n individuals chosen in accord with the study design.

DOSAGE ASSESSMENT AND RELATION TO HEALTH

The dosage, D, is the mass of pollutant that the subject accumulates during the study period T. For this discussion we will assume that inhalation is the only significant pathway for the material to enter the body during the period of the study. The dosage can be computed by Equation 8.

$$D = \sum_{i=1}^{4} \int^{T} (X_i - X_{eq}) v \phi(v) dt \qquad [8]$$

Where: X_i is the exposure in the ith category, $\mu g/m^3$
X_{eq} is the concentration of pollutant in equilibrium with the body fluids
v is the ventilation rate, m^3/min
$\phi(v)$ is the fraction of the theoretical mass transfer which is obtained, $0<\phi(v)<1$.

In general, exhaled breath will not be completely free of pollution since there may be insufficient time during a breath to absorb all the pollutant. For the case of carbon monoxide, CO, when X_i goes to zero there will be a net exhalation of CO when $X_{eq} > X_i$ (2). The health effect may also be dependent on the dose received per unit body weight, M. For the purpose of this analysis, we will assume that $\phi(v)=1.0$, $X_{eq}=0$, and that ΔHE is dependent on dosage D, although in practice one should compare the results of the experiment by correlating ΔHE with both D and D/M.

As in the case of linearly related exposure health effects, it can also be shown that if excess health effects are linearly related to $\bar{D}$, then measurement of $\bar{D}_n$ produces valid results when correlated with ΔHE.

In the past, several epidemiological studies have been performed as exposure experiments when the excess health effect observed was dependent on dosage. In these cases, the health effects were correlated with exposure instead of dosage, and, as a result, the true relation may have been hidden.

To demonstrate the difference between $\bar{X}_1$ and D, let us imagine a group of outdoor tennis players (A) being observed by sedentary spectators (B) with a constant k for all (A) and (B). During the match, the (A) group has a ventilation rate of 30 liters/minute, and the (B) group has a ventilation rate of 10 liters/minute. Both (A) and (B) have identical exposure in terms of $\bar{X}_1$, but (A) has three times the dosage of (B). On this day, if we study the health of these type (A) and (B) people, during a period ΔT, we might get results as shown in Figures 3A and 3B.

The plot of p(H) versus $\bar{X}_1$ shows variable health effects with a constant exposure, but the plot of p(H) versus $\bar{D}$ shows increasing health effects with an increase of dosage. Experiments have shown this type of relationship, where increasing exercise levels at constant concentration leads to increasing health effects of the subjects. The difference between $\bar{X}_1$ and D can be significant. Respiration and ventilation are at a minimum during sleep, which usually occurs at night. During the day, when active, the respiration and ventilation rates are higher. This relation is directly analogous to the diurnal variation of ambient pollution, which is usually minimum at night and maximum during the day. Consequently, there is a positive correlation between v and X_i and in general $\bar{D}/\bar{v}\ T>\bar{X}_E$, where $\bar{v}$ is the average ventilation rate. If ΔHE is analyzed with $\bar{X}_1$ instead of $\bar{X}_{E_n}$, the difference in results will be even greater.

In order to estimate the dosage $\bar{D}$, it is necessary to monitor the subject's activity and exposure to pollution. A table which could allow the computation of D for an individual may look something like Table 1.

By estimating the ventilation rate, v, and pollutant exposure, X_i, at each location, the integral of Equation 8 can be solved for D over the period of the study. A random sample of people can be studied, and as their exposures and activities are determined, the distribution p(D) can be estimated. As described previously for exposure, the necessary sample size for the dosage experiment is a function of the expected variation of X_i and v throughout the study community, the desired accuracy, and the designed confidence level. By taking a random sample of location of exposure and activity pairs, we can determine the mean dosage of the subjects, which is an estimate of the distribution mean.

The treatment of health data as being correlated with $\bar{X}_1$ instead of $\bar{D}$ may have contributed to the number of studies which produced nonstatistically significant results. The treatment of ΔHE as a function of $\bar{X}_1$ instead of D may also have contributed to the difficulty in reproducing results of epidemiological studies.

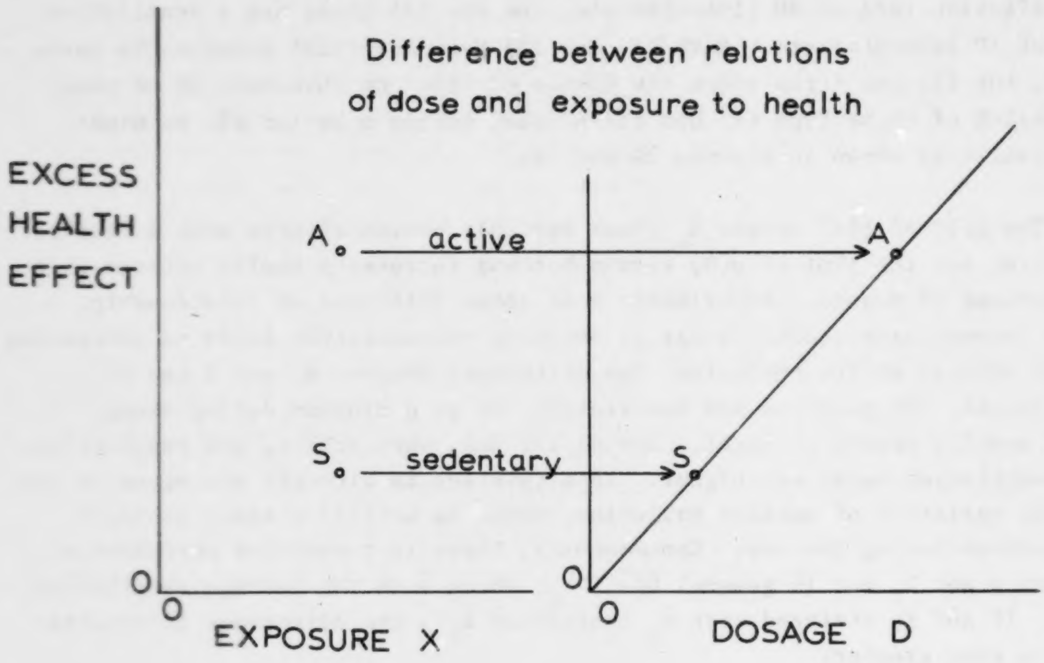

FIGURE 3A. Relation of excess health effect to pollution exposure.

FIGURE 3B. Relation of excess health effect to pollution dosage.

TABLE 1

Hypothetical Table of Activity and Location

TIME	LOCATION OF EXPOSURE	ACTIVITY
0000-0700	Home--indoors	Sleeping
0700-0800	Home--indoors	Light activity
0800-0900	In car to work	Sedentary
0900-1700	At office--indoors	Sedentary
1700-1800	In car to home	Sedentary
1800-1900	Home-outdoors	Light activity
1900-2100	Home--indoors	Sedentary
2100-2200	Jogging--outdoors	Very active
2200-2400	Home--indoors	Sleeping

SUMMARY

The design of epidemiological experiments needs to consider whether exposure or dosage of pollution is the independent variable. When dosage is the governing variable, the correlation between exposure and ventilation rate should be accounted for. Personal monitors can be used effectively to define the exposure distribution by a random sampling procedure, and ventilation can be estimated by knowledge of activity patterns.

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Discussion

BRAUN: David Braun, 3M Company. I enjoyed your paper very much. I would like you to comment, if you would, on the lung capture efficiency, because not all of the pollutant that we ventilate is captured by the lungs.

MAGE: That is correct. It is a variable for some pollutants. As a matter of fact, if your blood has higher COHb than the COHb which would be an equilibrium with the ambient CO, you won't take any CO in; you will exhale CO.

And the efficiency of captures of particles, for instance, is a function of the ventilation rate. I have oversimplified here purposely in that I assume my efficiency capture unit is constant. It is a variable that would have to be built in.

ZISKIND: Richard Ziskind, Science Applications. Do you think there might be any circumstances with something like sulfur dioxide or another pollutant that the body may respond to by developing brochoconstriction or something like that, so that you need to take that type of thing into account in the deposition of these pollutants?

MAGE: I am not a physiologist or a medical doctor, but I believe that those things are considered in all the analyses of the health effects which are produced.

Is there anybody here from health effects who would like to comment on that question?

STACY: Would you repeat the question?

ZISKIND: Dr. Mage is describing how you can measure ventilation for at least respiration rate and utilize that to help you come up with dose. And I was wondering that when you do get into an acute exposure, an episode of some sort, whether there are adequate indices or just that particular case where bronchoconstriction can occur or something like that that may alter deposition even of gases?

STACY: I think the answer to that is in the kind of information that does not exist. The biomathematics of the whole situation, the whole dosage situation, is very poorly understood. We don't know how much is caught up in the termination of noses, etc.

We know that in animals breathing ozone, part of it doesn't get down into the lungs.

With particulate matter, it depends entirely on the size of the particulate and the amount of ventilation. We just don't know how to model it yet.

ZISKIND: If you don't know how to model deposition, you can't go to the modeling of the effect of deposition.

STACY: The biomathematics of that situation is extremely crude at this time.

SCHEIDE: Gene Scheide, Environmetrics. You also have synergistic effects.

WHITE: Otto White, Brookhaven Laboratories. Two comments: one is that comparison in your model for exposure with the radiation data and to see whether or not you can predict a thousand dollars per person as being projected as the risk value in the radiation industry; the second comment deals with the linear dose response--I guess through all your relationships that there is no threshold effect. Could you comment on that?

MAGE: I haven't looked at the radiational calculations that you pointed out, but I would be pleased to if we can get together later.

As far as a zero threshold, this is just my assumption. There are people who see hockey sticks, that is, no effect below a certain value. It is quite controversial whether there is such a thing as a threshold.

When you consider that you have a control group which can have positive and negative deviations about their average response, and you compare it to people with low exposures, sometimes it is very, very hard to differentiate between no effect or no statistically significant effect.

Many times we have to have very large populations in order to get the power of the test to discern it. I have just chosen the simplest model.

STACY: Dave, I would like to hear you defend the statement you made a little earlier--that because most people are awake in the daytime, it would be better to have high pollution at night and low pollution in the daytime.

MAGE: OK, I will defend it to you as a member of the population who is concerned about the total number of people in the country who are exposed.

STACY: This is the question I am really asking: Should we be concerned about the average individual and his average exposure? Or should we be concerned about the worst case exposure?

MAGE: Let me give you a very clear definite answer: yes and no. Yes; we should as human beings. No; not if we are starting to look at economic evaluations, cost, and benefit. I mean, if there is only one person in the whole United States exposed to a particular level and it produces a health effect, it might be cheaper to give him or her $50,000 to move across town rather than spend a billion dollars to clean up the stack.

These are decisions that somebody other than myself will have to make. But these are also considerations that we have to look into.

DOCKERY: Doug Dockery, Harvard. You are concerned about the positive correlation between inhalation and air pollution levels in that you would breathe harder during high exposure.

I can't quantify this, but looking at our indoor-outdoor data and our personal monitoring data, in my experience people are involuntarily responding to the bad air pollution levels by doing things to clean up their homes.

And what we are seeing on the whole when we look across all our cities where we supposedly have a large difference in the air pollution levels--when we look at the indoor levels and what their exposure is--we see very, very small differences between this, because there has been this response of people not wanting to dust as often. So, they are closing up their houses and making other changes in their lifestyle to ameliorate their air pollution exposure.

And I think the actual case is just the opposite of what you are concerned about.

MAGE: The positive correlation I referred to arises because people are awake during the day and breathe at a faster rate. When pollution is higher during daylight hours, there is a positive correlation.

CHAPMAN: Robert Chapman, EPA. Dave, I was concerned where the previous discussion got left off by leaving in people's minds the impression that in certain types of epidemiological studies, it wouldn't be very useful to have an ongoing indication of what people's respiratory rate was.

I think it would be useful--very useful--in certain types of epidemiological studies for this reason: no matter whether one gets a clear indication of absolute dose from multiplying exposure times respiratory rate, one still can, I think, get some decent indication of relative dose between or among the people in the study on the grounds that the same type of pollution--and I realize what I am about to say is challengeable--within limits can be expected to affect all study participants in more or less the same way.

I know that there are a lot of holes in that statement. Still in all, I think that the uniformity of response would be enough so that if you do concentration measurements over the course of these people's exposure time, as well as their respiratory rate over the same time, you would get a considerably better indication of relative dose than we are able to get right now.

MAGE: Yes; I agree.

Carboxyhemoglobin Determinations from Expired Air

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Carbon monoxide is the most widely distributed and the most commonly occurring air pollutant. Total emissions of carbon monoxide to the atmosphere exceed those of all other pollutants combined (1). Carbon monoxide combines with hemoglobin to form carboxyhemoglobin (COHb). A new instrument called the Carboximeter was designed to measure this.

Hemoglobin has an affinity for carbon monoxide over oxygen of greater than 200 to 1; thus, it displaces oxygen, resulting in an interference with the oxygen transport system of the body. It also moves the oxygen dissociation curve to the left, binding the remaining oxygen more tightly. The predictability of carbon monoxide absorption and elimination in man makes the test for COHb a method of estimating ambient carbon monoxide levels to which a subject has been exposed. DHEW Secretary Califano's Office on Smoking and Health has started emphasizing the adverse health effects of carbon monoxide from tobacco smoke, which was highlighted in the recent Surgeon General's report. COHb and smoking are dose related, and the Office on Smoking and Health now uses a Carboximeter to demonstrate this immediate biological effect of smoking.

The heart appears to be the most vulnerable target organ for elevated COHb. Medical research has provided a new role for low-level COHb in heart disease.

Some of these adverse health effects have been measured at only slightly elevated COHb levels (2). For instance, levels of about 2 1/2 percent have been shown to aggravate angina and depress the forcefulness of contraction. Levels of about 3 percent have been shown to aggravate intermittent claudication. Electrocardiograms have been altered in normal subjects at about 8 1/2 percent COHb. Thus, with this kind of medical evidence available, the measurement of COHb has become increasingly important. Most of the well-known symptoms of carbon monoxide poisoning such as headache, nausea, etc., do not occur below the 15 to 20 percent COHb level. Thus, we are usually unaware of elevated levels in these lower ranges, and a diagnostic test is necessary to make that determination.

Traditionally, the test for COHb has been difficult to make. It requires drawing blood and performing blood gas analysis on equipment that requires expert calibration and highly trained personnel to operate it. It is usually in a location remote from the patient, resulting in delays from sample to results. It may not always be convenient to take a blood sample, and the sample must be properly prepared and transported. All in all, these traditional tests are not suitable for field use or for applications where portability or on-the-spot results would be necessary. Thus, the rarity of obtaining COHb measurements, even when they might be useful. An alternate method of obtaining rapid COHb levels is clearly needed. The well-known Haldane equation expresses the relationship between alveolar CO and COHb. This relationship was used by Dr. Sjostrand (3) to determine COHb from alveolar CO.

In 1958, Dr. Jones (4) demonstrated that CO tension in the alveoli will approximate the CO tension in the pulmonary capillaries using a 20-second breath holding technique. In this technique, the air in the lungs is expired, then a deep breath is held for 20 seconds. It is necessary to expire all the air from the lungs and collect the last portion of air from the alveoli. The alveolar CO is then measured. Using this technique, Jones demonstrated an almost linear relationship between alveolar CO and COHb. Several other studies using the Jones 20-second breath holding technique have corroborated this relationship. Two curves derived from such studies are shown in Figure 1 and compared to the curve of Dr. Jones. One is from Dr. Peterson (5) and the other from Dr. Stewart (6). These are best-fit curves from multiple data points. Dr. Peterson derived the formula shown, and it is this formula which we have selected to use for conversion of alveolar CO to percent COHb. With this alveolar CO-COHb relationship well established, it was necessary to develop an instrument that would measure alveolar CO accurately and reliably, not only under lab or clinical conditions, but in field situations where portability is important.

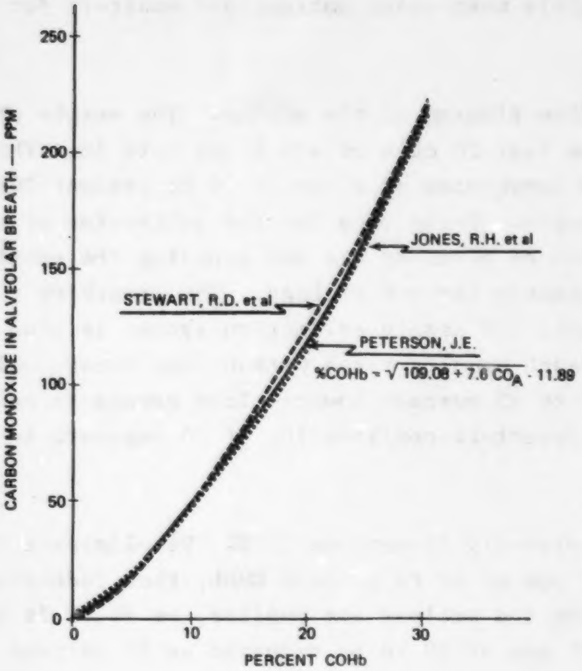

FIGURE 1. The relationship between alveolar CO and COHb after 20-second breath holding.

Theoretically, any instrument that can measure CO in air could be used to measure COHb by the expired-air technique. However, there are many potential areas for error if an ambient CO monitor is used. The Ecolyzer, with its accuracy, ease of calibration, and portability, has become one of the most popular instruments for measuring CO in ambient air. Indeed, it has been used to measure expired air CO for conversion to percent COHb.

The sensor has excellent linearity accuracy and repeatability, and a minimum detectable sensitivity of .5 ppm. Thus, it has the ability to reliably read low concentrations and to measure normal COHb levels. For example, 1 percent COHb--the approximate average normal for nonsmokers--represents only about 7 ppm of CO in expired air. This is a result of red cell destruction and breathing naturally produced CO in ambient air.

Recognizing the need for a new instrument to measure COHb by the expired-air technique, we joined with Energetics Science to design this new instrument with the advantages of the sensor but without the disadvantages of the ambient air monitor for this procedure. We designed out several areas of potential error possible when using ambient air monitors for making the COHb test.

Figure 2 is a flow diagram of the system. The sample chamber is designed to collect the last 20 cc's of air blown into it. This is important because the accurate conversion of alveolar CO to percent COHb requires a good alveolar air sample. Using bags for the collection of expired air samples risks dilution of alveolar air and exposing the sample to ambient CO. Our system eliminates the use of bags. The breathing technique for blowing the sample into the sample collection system is also simplified. However, nonalveolar breath samples taken without the breath holding technique are usually about 10 to 15 percent lower--close enough to make the instrument useful in obtaining immediate confirmation of CO exposure in uncooperative subjects.

Our readout is directly in percent COHb. We eliminate the need to convert the readings of ppm of CO to percent COHb, thus reducing the potential for error. When using the ambient air monitor, we found it quite common for a reading of, say, 20 ppm of CO to be recorded as 20 percent COHb.

We have added an automatic scale change on our dual scale. One scale is zero to 10 percent COHb, and the other is zero to 33 percent. When the reading goes over 10 percent, the needle will automatically move to the larger scale, and a light will indicate that that scale should be read. When the instrument is reset, it automatically goes back to the smaller scale. This of course reduces the risk of reading the wrong scale. A sample-and-hold circuit allows for proper reading and recording results. The peak CO in the sample is measured and the meter indicates percent COHb, holding the reading until the instrument is reset.

We isolate the alveolar air sample by use of a zero filter on the outboard end of the sample chamber. Thus, when we pump the sample from the sample chamber to the sensor, all ambient CO is removed, and the only CO to reach the sensor comes from the lungs.

We have moved the high voltage outside the case with a UL-approved battery charger, but we have retained the portability with rechargeable batteries. The instrument can be used in its portable mode for up to 8 hours.

There are other design considerations that I will mention briefly.

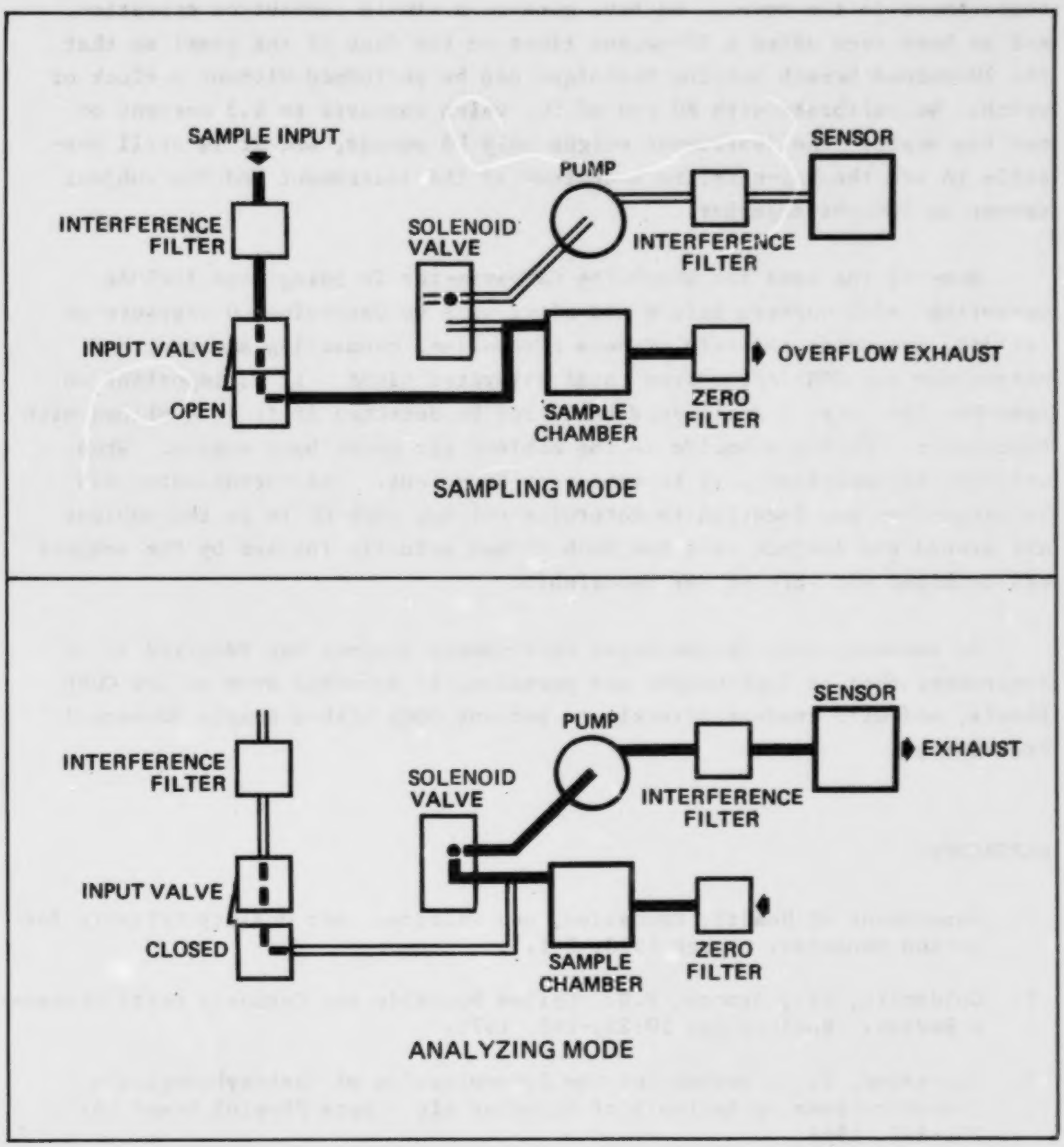
SAMPLE INPUT
INTERFERENCE FILTER
INPUT VALVE
OPEN
SOLENOID VALVE
PUMP
SENSOR
INTERFERENCE FILTER
OVERFLOW EXHAUST
ZERO FILTER
SAMPLE CHAMBER
SAMPLING MODE
INTERFERENCE FILTER
INPUT VALVE
CLOSED
SOLENOID VALVE
PUMP
SENSOR
EXHAUST
INTERFERENCE FILTER
ZERO FILTER
SAMPLE CHAMBER
ANALYZING MODE

FIGURE 2. Flow diagram of the system.

We have angled the meter to make it easy to read and have added a carrying compartment in the cover. We have gone to a simple pushbutton operation, and we have even added a 20-second timer on the face of the panel so that the 20-second breath holding technique can be performed without a clock or watch. We calibrate with 20 ppm of CO, which converts to 4.3 percent on our top scale. The instrument weighs only 10 pounds, and it is still possible to use the bag-sampling technique if the instrument and the subject cannot be brought together.

Some of the uses for which the Carboximeter is being used include: measuring shift workers before and after work to determine CO exposure on the job, measuring the rate of heme catabolism, counseling smokers, and correcting for COHb error from total saturated blood. It is important to remember that even a small dose of CO can be detected if it is combined with hemoglobin. Carbon monoxide in the ambient air never hurt anyone. When attached to hemoglobin, it becomes very dangerous. The Carboximeter can be carried to any location to determine not how much CO is in the ambient air around the subject, but how much CO was actually inhaled by the subject and combined with his or her hemoglobin.

In summary, this Carboximeter development project has resulted in an instrument that is lightweight and portable, is accurate even at low COHb levels, and will readout directly in percent COHb with a simple 30-second breath test.

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Discussion

MAGE: Is there any restriction in the amount of expired breath that is necessary? I am interested in school children; how small a child can use this device and this technique?

TOMLINSON: One of the reasons we made the sample chamber so small is for that very reason--so that we would not require a large sample. Almost anyone who is capable of breathing into the instrument, regardless of the size of his lungs, can get a big enough sample, a 20 cc sample, out of it.

As a matter of fact, this is being used in schools right now for smoking education. And the kids love it. They have no problem using it. They blow into it, and we are getting excellent results in that kind of application.

ZISKIND: Richard Ziskind, Science Applications. A couple of questions: first, could you tell us anything about the school children levels of CO you are defining compared to an adult level?

TOMLINSON: We have found that generally speaking, the carboxyhemoglobin levels are--with the kids who smoke--above what we would find in adults. I don't have all the data with me, but that is the overall look of it.

What is amazing is that the smoking age keeps going down. We get kids smoking in the fourth, fifth, and sixth grades.

ZISKIND: Another question: I have seen one study that indicates a variation in regression coefficient between alveoli CO level and carboxyhemoglobin which suggests that before doing any survey--especially if you are going to look at many people and contrast, say, two groups such as control and exposure--that they would recommend direct blood analysis be made at least on some proportion of that population that they are going to look at.

Would you think that is not necessary?

TOMLINSON: Well, we have done quite a number of tests on fairly large groups of people. We have done bloods on the original development of this with very good correlations.

As a matter of fact, Dr. Anderson at the University of Louisville has two of these instruments. He reported to me last April that he was getting a .96 correlation of bloods done on the new IL-282. The old 182 was not very reliable for COHb, but the 282 is pretty good.

ZISKIND: What is the price?

TOMLINSON: $3,500.

SPENGLER: I have done a lot of carboxyhemoglobin tests as you described with an Ecolyzer and found that I had a lot of problems with someone who had recently used an alcohol mouthwash. If any volatile stuff was ingested previous to the test, an instrument would give a positive reading for a long period of time--sort of poison the action for a while.

Have you eliminated that problem?

TOMLINSON: The interference filter in the mouthpiece assembly is primarily for alcohol. It will absorb a lot of it. There is a simple test to determine when the filter begins to pass alcohol, but that is in calibration gas through it.

But you are right; it will do that. If a guy has a "two martini lunch," even the mouthpiece filter will not take it out if it is used after the ingestion.

That is a problem. Particularly in exhibitions, in trade shows, people come around after lunch and say, "I want to blow into your machine." And it is very difficult to explain their responses.

Intelligent Personal Physiologic Monitors in Clinical Environmental Health Effects Research (Part I)

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INTRODUCTION

The lack of a definitive data base in urban environmental health effects research (2,9,12,13,18) today is based to a large extent on systems and devices representing extensions of hospital-oriented biomedical instrumentation. These devices are frequently designed as vital sign detectors for patients with well-developed physiologic symptoms; i.e., known cardiac history, emphysema, post-surgical recovery, and the acutely ill. Devices of this type serve in life-saving roles and need not have the sensitivity to detect subtle physiologic changes. Detection of subtle physiologic changes in a normal, healthy, urban population requires considerable clinical judgment as a means of screening out false positives. As such, conventional biomedical instrumentation may not be adequate for assessment of subtle changes in normal, mobile, healthy adults exposed to environmental pollutants. Conventional biomedical instrumentation systems may be useful in clinical health effects research as baseline reference measuring devices. However, the subject must be brought to the clinic, thus limiting the population under study. The problem in urban personal monitoring requires incorporating the biomedical and pollutant instrumentation on-board the attire of the test subject as a means of data collection (12). The bulk, size, weight, power, and lack of subtle detection sensitivity, and the lack of portability of conventional hospital-like instruments, are incompatible with clinical epidemiologic research. Ideally, health effects protocols designed to search out dose-response relationships must be extended from the clinical research laboratory to the field through implementation of properly designed "personal monitors." The rationale of present-day clinical protocols does not lend itself to personal monitoring, in view of the high degree of test-subject mobility and normal function in daily activities.

The above limitations have precluded the design and implementation of clinically useful systems and, in effect, have limited the urban health effects data base. In order to circumvent the above limitations, a quantum jump in the scientific design of biomedical instrumentation, transducers, and pollutant dosimeters is imperative. Successful clinical epidemiologic research, therefore, must be based on highly individualized noninvasive techniques, interactive software systems, transducers, and highly sophisticated systems managers in the form of microcomputers, all on-board the mobile urban test subject as exemplified in Healthe-Belt (12).

It is, therefore, the objective of this paper to establish a series of basic and fundamental guidelines toward the design of environmentally useful personal monitors, as opposed to classic hospital-like devices used in clinical research. In view of the limitations of previous technology (9,13), this design initiative is set forth herein through illustration of several design examples requiring a significant change in operational and clinical philosophy. Several new and original concepts are introduced which take advantage of the modern measurement technology, very large scale integration (VLSI), and microcomputers (14,15,17), today and in the near future.

DESIGN STRATEGY FOR INTELLIGENT PERSONAL PHYSIOLOGIC MONITORS (IPPM)

Dose-response measurements on a normal individual performing daily activities or work tasks within his/her environment must be based on two major elements in order to represent credible and scientific health effects data. These elements are the simultaneous measurement and documentation of pollutant dose level and concomitant physiologic response. This philosophy must be recognized as fundamental to any health effects research (9,12,13). Further, this concept is the cornerstone of any management strategy in the design of any personal monitor system in support of scientifically credible legislation. Since design of pollutant dosimeters is an extensive subject beyond the scope of this paper (18), only the physiologic data acquisition system designs will be addressed herein.

Clinical epidemiologic requirements for personal monitors are broad and extensive. In order to introduce and establish the roots of a new design philosophy (4,11,12), a series of design priorities are identified to illustrate the need, criteria, and methodology in attaining a quantum jump (11) in system design required for EPA to fulfill its part in any Public Health Initiative through intelligent personal physiologic monitors. Design of personal monitors must include the following priorities:

- Test subject comfort and wearability;
- Design of clinical data base;
- Design of new physiologic parameters;
- Design of new multimode transducers;
- Design of new algorithms to replace conventional electronic circuits;
- Design of clinical field logistics and the means to clinically validate and characterize system performance with clinical and air pollutant standards.

USER DESIGN CRITERIA FOR INTELLIGENT PERSONAL PHYSIOLOGIC MONITORS

The EPA/Health Effects Research Laboratory response to the Office of Health Effects mandates imposes the need for significant scientific flexibility in collection of desired data base knowledge in support of preventive environmental medicine and proposed legislation. This requirement, coupled with the advancements of medicine and technology, creates the need for the ever-changing variety of multivariable protocols which have become a fact of life in health effects research. Conversely, no organization can afford to re-tool its scientific resources each time a new research issue or pollutant episode develops. This is particularly critical in assessing environmental episodes and concomitant health effects data. Clinical research in the past has advocated the design of new systems and devices to suit specific protocols wherein the design cycle time is incompatible with pollutant episodes and the need to characterize related health decrements. Frequently, when such systems transfer from the development stage to the clinical-use stage, they are often obsolete or the protocols have been changed to answer new research questions. Therefore, utilizing conventional hospital biomedical instrumentation in this type of research climate would render these systems almost useless. In order to illustrate the type of design flexibility envisioned by the clinical investigator, the following criteria depict a few guidelines necessary for a quantum jump in design of IPPM systems.

User Design Criteria

1) Design a legislatively defensible data base as a first-line scien-

tific priority before any system designs are attempted.

2) Design means for software flexibility in protocol changes so as to support the data base product.

3) Provide protocol flexibility through adaptive software designs and elimination of hardware wherever possible.

4) Incorporate modularized prescription design for ease of protocol adaptability.

5) Provide means of protocol replication by others through very large scale integrated circuit memories erasable programmable read only memories (EPROMS).

6) Design anatomically comfortable transducers which provide a natural interface to male and female test-subject anatomy.

7) Design multimode transducers to acquire more than one parameter from a given anatomic site and reduce subject encumbrance.

8) Design "intelligent transducers" which are capable of sensing physiologic data and converting these data into meaningful clinical measurements prior to reporting on call to a higher-level system.

9) Incorporate multimode statistical data base at the system level to avoid extensive redesign of data base at the end of a given study.

10) Design standardized modular systems and sensors which are interchangeable and adaptable to several protocols and/or research questions.

11) Maintain fixed hardware while software provides the key flexibility and is varied to suit new research questions.

12) Ensure that system size, weight, power, and interfacing are compatible with normal human activities and acquisition of scientific data.

13) Ensure cost effectiveness through anticipatory design in support of high-volume disposal IPPM systems.

14) Replace conventional (TTL) circuit logic with microcomputerized algorithms performing circuit logic functions wherever possible.

15) Design all systems in direct anticipation of changing needs and minimize technological obsolescence when protocols or programs are changed.

INTELLIGENT PHYSIOLOGIC PERSONAL MONITOR (IPPM) MK-I

Intelligent personal physiologic monitors represent a significant departure from conventional clinical instrumentation in that IPPM devices (11,12) are designed to respond to noninvasive environmental health effects needs and not life-saving functions. The key design factors identified above are reflected and illustrated in the design approach described here.

The design approach to IPPM systems and devices must be based on multilevel modular designs geared to the ever-changing and accelerated technology of today and to that of the next 5 years. It is not uncommon today to initiate a given systems design effort only to find protocols were changed or became obsolete 18 months later when the device was completed. It is, therefore, imperative that the design structure advocated must be constantly and continuously adaptable to changing needs throughout the design and development cycle. The most effective approach to adaptive design is through flexible microcomputer software. Previous technology (9,10,13) has not been responsive to this design philosophy and has resulted in a multitude of surplus instruments or hardware designs for each protocol or each new research question. Conversely, hardware logic has its place in many endeavors. However, the bulk, size, power, and weight of sensors and instrumentation would pose considerable constraints on human anatomy by conventional design methodology. Clinical criteria, changing protocols, new research questions, cost effectiveness, and the need for mass clinical epidemiologic screening of the population demand a "revolutionary change" in overall design approach of physiologic data acquisition systems (PDAS) for any clinical research. The major attributes of any PDAS system design (12) responsive to the above criteria and, specifically, to health effects personal monitors, are "clinical flexibility," "test subject comfort and acceptance," and "cost effectiveness." The design of these attributes begins with interfacing the human anatomy to the physiologic transducer (8).

ANATOMY-TO-TRANSDUCER INTERFACE

Considering today's technology, particularly very large scale integration of the next 3 to 5 years (14,15), the most promising approach in design of personal monitors is clinically interactive software which emulates hardware logic functions in concert with human judgment. By imparting interactive human judgments or clinical rationale to the processing of health effects data, we impose a level of human intelligence as an inherent function of the system design. Hence, the name "intelligent personal physiologic monitors."

The efficacy of any PDAS system is based on the type of analog signals available which represent the range of human variance to be analyzed and documented in a given data base design.

IPPM devices are unique in that five major constraints are imposed on the designer and the clinical researcher. These are:

- All transducers and measurements must be noninvasive and painless.
- The need for subject freedom, comfort, and ease of wearability without loss of scientific data is imperative to the success of IPPM.
- Significant limitations exist in the interfacing of noninvasive transducers to both male and female anatomy in search of valid physiologic parameters.
- Size versus function is a matter of technological trade-offs as contrasted against a definitive data base design.
- Cost effectiveness must permit mass production in order to reach statistically significant populations in support of any EPA Public Health Initiative.

The significant constraints of human anatomy demand and impose the acquisition of multimode physiologic transducers from the minimal number of anatomic placements; i.e., multimode transducers (11) should provide two or more parameters from a common transducer. Hence, time-shared transducers represent a realistic approach in multiparameter sensing, which may jointly aid in characterizing physiologic decrements resulting from air pollutants. However, multimode transducers impose a dilemma of excessive amounts of data, that are frequently beyond human comprehension, being produced. The significant need herein for an IPPM is the ability to screen multimode parameter variance based on previous human judgment and clinical criteria to the extent of reducing transducer outputs to an interim-processed level. This endeavor may be feasible through specifically designed "intelligent physiologic transducers" (IPT) (4,11). IPT devices serve to screen out irrelevant data and only utilize responses which have met a level of interactive judgment through the rationale of clinical software protocols. The criteria and clinical rationale would be a function of the microcomputer algorithms within the transducers themselves. Hence, in higher-level PDAS memory systems, such an IPPM would not be saturated with useless data, thus clogging the support of an effective and defensible data base--as is the case in some clinical laboratory PDAS systems in existence today.

The Concept of Transphysioware

The design of IPT devices advocated here is based on transducing (8) a given physiologic signal from the human anatomy into its analog form. However, the need is to convert the analog signal into some meaningful clinical measurement which requires a form of clinical judgment; i.e., transduce a physiologic function signal into a meaningful clinical measurement. Imparting the latter judgment to a transduced signal can be accomplished, within limits, through an appropriate algorithm. This process is defined here as "transphysioware" (11). This function is advocated at the transducer level by incorporation of a microcomputer within the transducer itself. Ideally, limited screening of data would occur at the transducer level, thus simplifying the process function of the IPPM whose priorities and memory capacity is spread over several other physiologic and air pollutant dosimeter parameters.

Advocating a specific philosophy in any endeavor is best illustrated by realistic examples which address the principles, problems, and efficacy of design integrity. The key design factors identified above are reflected and illustrated in the following example designs.

DESIGN EXAMPLE

Multimode Respiratory Intelligent Personal Physiologic Monitor

Preliminary pulmonary function studies within EPA suggest that exercise respiratory tidal volume and heart rate provide a means of characterizing pulmonary reactivity to pollutants to the extent that subtle changes in overall lung function are detectable. Clinical studies currently underway in the EPA CLEANS facilities have served to develop the clinical rationale in respiratory tidal volume measurement. However, these protocols are precluded from use at an IPPM level. The design issue is: how to extend a respiratory tidal volume protocol to a personal monitor level. A preliminary design of such a system at an IPPM level is illustrated in the subsequent design.

A dedicated single chip 2K memory microcomputer (Intel 8748/8749) and supportive preprocessing are employed in a preliminary IPPM design as follows:

1) A pneumotachograph for measurement of respiratory flow is incorporated into a construction worker's helmet.

2) The transducer is normally recessed in a frontal storage area and is pulled out with the index finger by the subject on software auditory beeper command.

3) The subject places the pneumotachograph in his mouth (for a predetermined period) and continues performing his duties.

4) The microcomputerized IPPM is preprogramed to present the subject with a previously validated protocol based on a sequence command after the pneumotachograph is placed in the subject's mouth.

Figure 1 illustrates a timing chart of multimode parameters desired in a typical exercise tidal volume protocol wherein only one transducer is used for pulmonary measurements. (With multimode parameters, one anatomic placement is used.) The clinical interactive rationale provided in the software algorithm provides four parameters; i.e., respiratory rate, volume, flow, and tidal volume, or a total of four parameters from one transducer placement. The algorithm converts respiratory flow to volume by mathematical integration of the flow signal. Each flow breath rate and volume signal is stored in RAM memory and displayed in an accumulative form over a 1-minute period, resulting in a measure of tidal volume (see Figure 1). On a separate channel, heart rate trend is recorded and constantly compared to the prescribed clinical safety level within the algorithm for a given subject's age and maximum heart rate. Hence, the 8748 microcomputer algorithm performs an interim level of processing, thus providing the IPPM with trend information permitting clinically meaningful judgment in detection of subtle changes; i.e., a transducer has sensed the physiologic signal, and a microcomputer algorithm has converted one signal into four meaningful clinical parameters (transphysioware) as health effects indicators. If preset trend levels exceed prescribed levels of heart rate, a flag and alarm to "halt" the test subject from further effort are initiated, and the IPPM accesses the respiratory IPT for relevant data in support of a dose-response data base.

Figure 2 illustrates a preliminary record of the actual 8748 microcomputer controlled analog signals and digital measurements. Figure 3 illus-

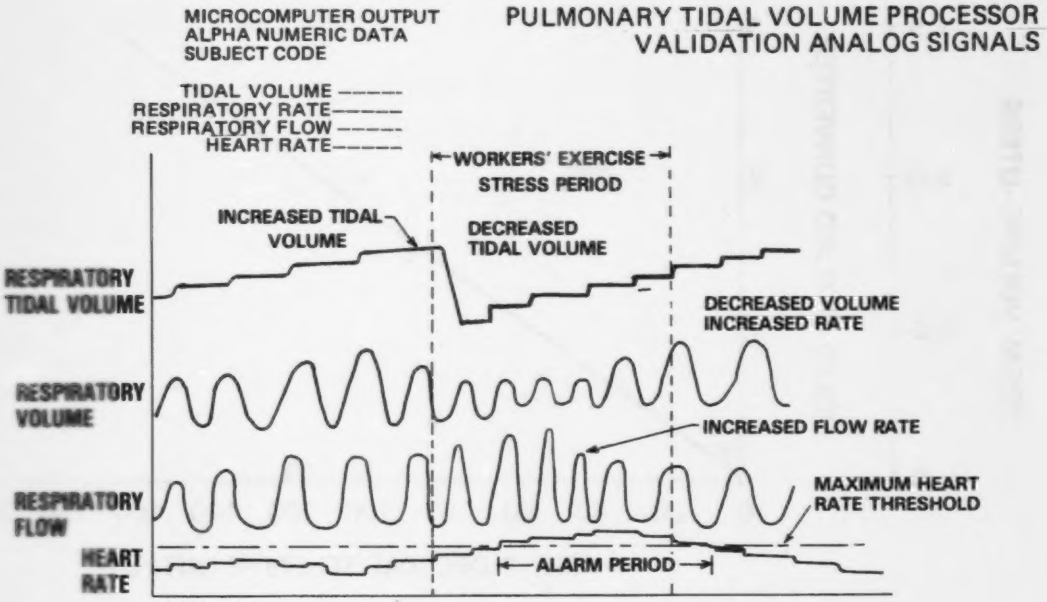


FIGURE 1. Ideal pulmonary function parameters from one transducer, 8748 microcomputer algorithm process. Heart rate, separate transducer.

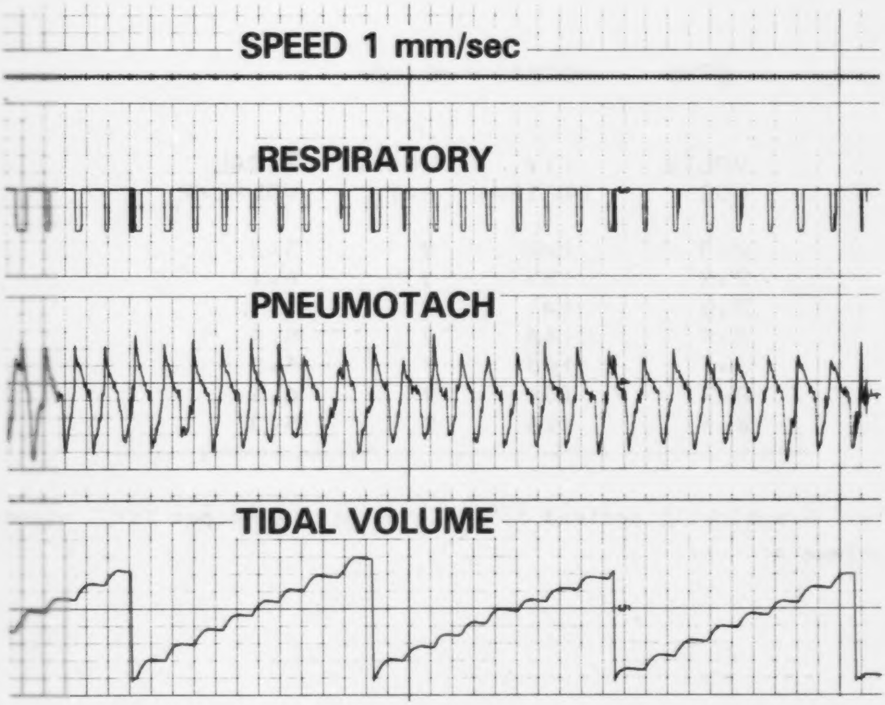


FIGURE 2. Actual human pulmonary record. Top, respiratory rate (digital). Middle, respiratory flow. Bottom, respiratory tidal volume. See calibration curve, Figure 3.

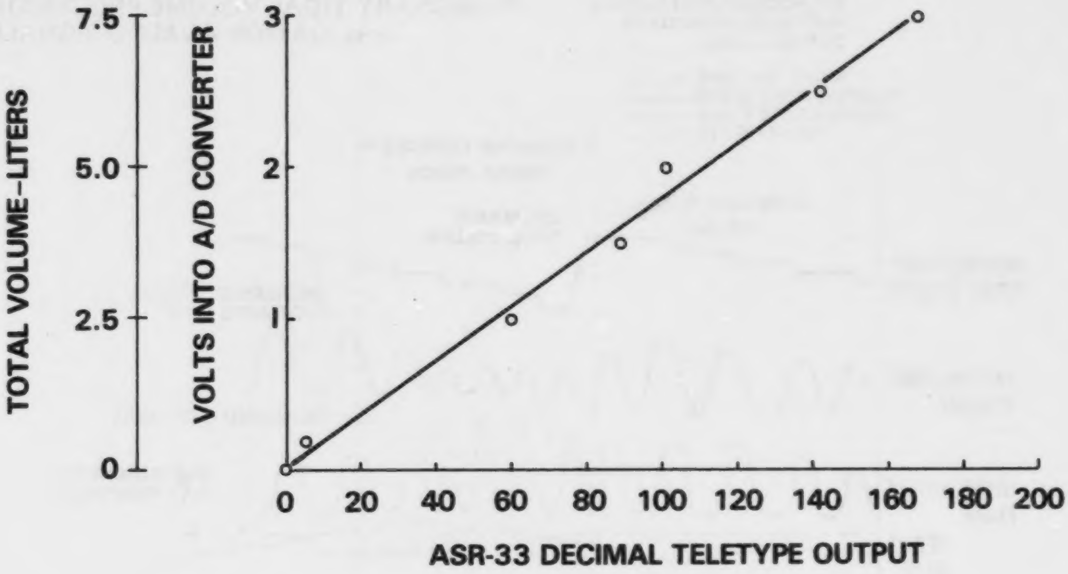


FIGURE 3. Respiratory pneumotach calibration based on Fisher-Porter Flow Meter Model 10A1027A. System calibration includes A/D Converter and 8748 microcomputer.

```
8748     MICROCOMPUTER

VOLTS     TTY      RESP.   TIDAL
ADC     DECIMAL    RATE    VOL/L/M

2.3       140       7       5.8
2.8       157       7       6.1
2.3       141       7       5.1
2.9       160       7       6.8
3.1       163       7       6.9
2.7       158       7       6.6
2.6       156       7       6.3
```

FIGURE 4. Graphically derived 8748 microcomputer output for 1 minute of tidal volume at rest.

trates the calibration of the pulmonary tidal volume IPPM system used to produce the record of Figure 2. Figure 4 illustrates the microcomputer output parameters computed during a 1-minute sample. Figure 5 illustrates a possible configuration of a pulmonary IPPM built into a construction worker's headgear. Figure 6 illustrates design details of the exercise pulmonary tidal volume processor contained in a construction worker's helmet.

DESIGN EXAMPLE

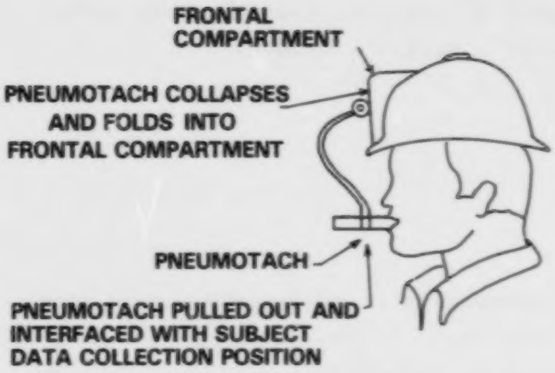
Multimode Cardiopulmonary IPPM

Static cardiovascular measurement assessment of young normal test subjects exposed to air pollutants may be difficult in terms of detecting subtle change responses. Conversely, as in exercise pulmonary function, potential for cardiac dose-response processing may be feasible through the appropriate selection of the parameters and trend analysis.

Several cardiac parameter measurements (1,3) may be required in order to accumulate a sufficient battery of data to establish correlation of subtle trends or a dose-response index following pollutant episodes. As an example, a current EPA system development study involving acquisition of cardiac (treadmill exercise) systolic time intervals (STI) (a measure of myocardial contractility) has demonstrated that STI measurements may be highly applicable for field IPPM systems. The clinical validation of cardiac impedance measurements has been well documented in the literature by Kubicek, Kizakevich (5,6,7), and others. Definitions are beyond the scope of this paper and are contained in the referenced literature (5,6,7,16,19). The multiplicity of cardiac parameters available from impedance cardiography currently in development at EPA/CSD clearly indicates the potential for use in IPPM systems. (See Table 1.) Figure 7 illustrates a male electrode configuration for impedance cardiography wherein STI provides an index of aortic impedance blood flow velocity and aortic left ventricular ejection time (LVET) (5,6,7). From these two basic cardiac measurements, it is possible through clinical rationale to develop several parameters which give further insight to variations in normal cardiac performance. Figure 8 illustrates a real time microcomputer display of heart rate during a "Bruce" exercise protocol. The display incorporates a medical-legal safety monitor for heart rate (see 85 percent max) and a heart-rate trend throughout the protocol period.

An Intel 8010 single board microcomputer functions as a system controller

(INTELLIGENT)
EXERCISE PULMONARY TIDAL VOLUME PROCESSOR
(CONSTRUCTION WORKER)

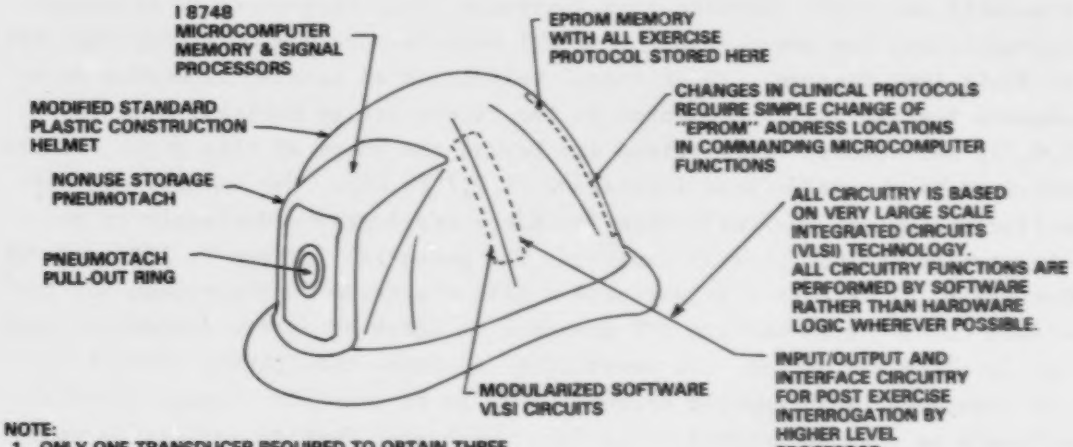

FRONTAL COMPARTMENT
PNEUMOTACH COLLAPSES AND FOLDS INTO FRONTAL COMPARTMENT
PNEUMOTACH
PNEUMOTACH PULLED OUT AND INTERFACED WITH SUBJECT DATA COLLECTION POSITION

NOTES:

- TEST SUBJECT PERFORMS HIS NATURAL ON-THE-JOB WORK WITHOUT ENCUMBERANCE.
- THREE AUDIO BEEPS ALERT THE SUBJECT TO PULL OUT PNEUMOTACH (1) SENSOR AND PLACE IN HIS MOUTH UNTIL TWO AUDIO BEEPS ARE HEARD IN WHICH HE STOPS AND RESTORES THE DEVICE IN THE HELMET.
- MICROCOMPUTER AND SIGNAL PROCESSING CIRCUITRY CONTAINED WITHIN STORAGE SPACE OF CONSTRUCTION HELMET.
- ALL ALGORITHMS FOR PHYSIOLOGIC SIGNAL QUANTITATION ARE CONTAINED IN EPROMS RESIDENT IN EACH SUBJECT'S SYSTEM; i.e., ALL CLINICAL PROTOCOLS IDENTICAL IN EACH SYSTEM.
- ALL PROTOCOLS PREVIOUSLY VALIDATED IN CLEANS PROTOCOL DEVELOPMENT PRIOR TO EPIDEMIOLOGIC FIELD USE.

FIGURE 5. Proposed tidal volume IPPM configured into construction worker's helmet. Note details.

EXERCISE PULMONARY TIDAL VOLUME PROCESSOR
MARK I PROTOCOL


I 8748 MICROCOMPUTER MEMORY & SIGNAL PROCESSORS
EPROM MEMORY WITH ALL EXERCISE PROTOCOL STORED HERE
MODIFIED STANDARD PLASTIC CONSTRUCTION HELMET
NONUSE STORAGE PNEUMOTACH
PNEUMOTACH PULL-OUT RING
MODULARIZED SOFTWARE VLSI CIRCUITS

CHANGES IN CLINICAL PROTOCOLS REQUIRE SIMPLE CHANGE OF "EPROM" ADDRESS LOCATIONS IN COMMANDING MICROCOMPUTER FUNCTIONS

ALL CIRCUITRY IS BASED ON VERY LARGE SCALE INTEGRATED CIRCUITS (VLSI) TECHNOLOGY. ALL CIRCUITRY FUNCTIONS ARE PERFORMED BY SOFTWARE RATHER THAN HARDWARE LOGIC WHEREVER POSSIBLE.

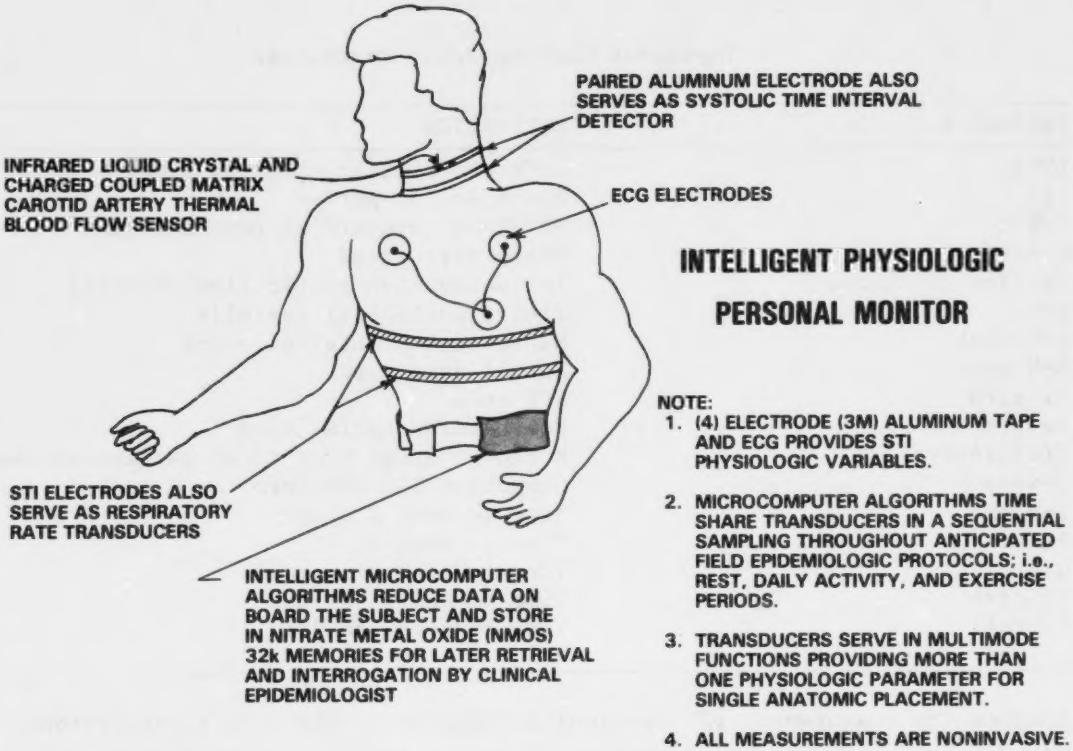
INPUT/OUTPUT AND INTERFACE CIRCUITRY FOR POST EXERCISE INTERROGATION BY HIGHER LEVEL PROCESSOR

NOTE:

1. ONLY ONE TRANSDUCER REQUIRED TO OBTAIN THREE RESPIRATORY VARIABLES; i.e., PNEUOMOTACH FLOW IS CONVERTED TO VOLUME AND TIDAL VOLUME MEASUREMENTS THROUGH MICROCOMPUTER ALGORITHMS.

2. HEART RATE REQUIRES ITS DEDICATED TRANSDUCER WHILE MICROCOMPUTER ALGORITHM PROCESSES HEART RATE AND SETS MAXIMUM HEART RATE THRESHOLDS FOR INDIVIDUAL'S AGE; i.e., CLINICAL LEGAL SAFETY. IF HEART RATE EXCEEDS PRESCRIBED RANGE, AN ALARM IN THE FORM OF AN AUDITORY BUZZER GOES OFF IN HELMET.

FIGURE 6. Design details and features of construction helmet.


PAIRED ALUMINUM ELECTRODE ALSO SERVES AS SYSTOLIC TIME INTERVAL DETECTOR
INFRARED LIQUID CRYSTAL AND CHARGED COUPLED MATRIX CAROTID ARTERY THERMAL BLOOD FLOW SENSOR
ECG ELECTRODES
STI ELECTRODES ALSO SERVE AS RESPIRATORY RATE TRANSDUCERS
INTELLIGENT MICROCOMPUTER ALGORITHMS REDUCE DATA ON BOARD THE SUBJECT AND STORE IN NITRATE METAL OXIDE (NMOS) 32k MEMORIES FOR LATER RETRIEVAL AND INTERROGATION BY CLINICAL EPIDEMIOLOGIST

INTELLIGENT PHYSIOLOGIC PERSONAL MONITOR

NOTE:

1. (4) ELECTRODE (3M) ALUMINUM TAPE AND ECG PROVIDES STI PHYSIOLOGIC VARIABLES.
2. MICROCOMPUTER ALGORITHMS TIME SHARE TRANSDUCERS IN A SEQUENTIAL SAMPLING THROUGHOUT ANTICIPATED FIELD EPIDEMIOLOGIC PROTOCOLS; i.e., REST, DAILY ACTIVITY, AND EXERCISE PERIODS.
3. TRANSDUCERS SERVE IN MULTIMODE FUNCTIONS PROVIDING MORE THAN ONE PHYSIOLOGIC PARAMETER FOR SINGLE ANATOMIC PLACEMENT.
4. ALL MEASUREMENTS ARE NONINVASIVE.

FIGURE 7. Typical STI cardiac impedance electrode configuration, male subject.

wherein the "R" wave of the electrocardiogram (ECG) triggers an algorithm to perform ensemble averaging of the aortic impedance signal. Figure 9 illustrates a typical output supported by multiple parameters depicting an index of myocardial contractibility through computation of systolic time-interval measurement during treadmill exercise conditions. Figure 9 illustrates an ensemble-averaged aortic impedance signal recorded under conditions of walking, jogging, and deep knee bends--conditions thus highly applicable to mobile urban subjects. A microcomputer algorithm eliminates the classic artifact, resulting in a clean, clinically useful waveform.

Figure 10 illustrates a trend plot of selected variables which have potential for detection of subtle changes induced by air pollutant exposure.

Figures 8 through 10 illustrate the measurement of STI's on a male subject. However, the efficacy of a scientific statistical data base must

TABLE 1

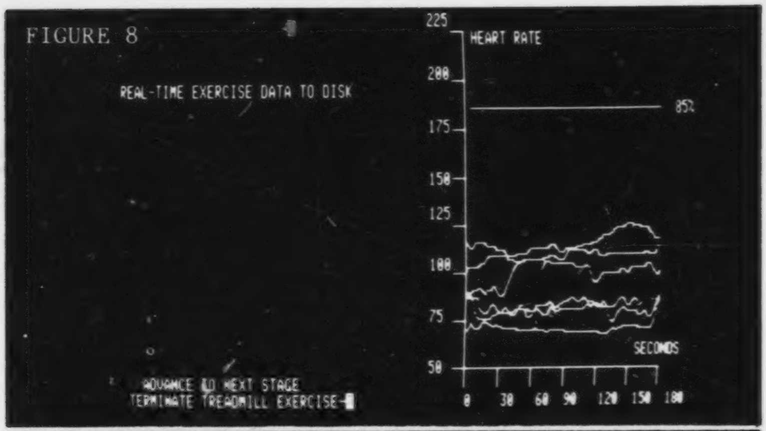
Impedance Cardiographic Parameters

PARAMETER	DEFINITION
LVET	Left ventricular ejection time
PEP	Pre-ejection period
Ratio	PEP/LVET, myocardial contractility
Heart rate	Heart rate trend
Cardiac impedance	1st derivative aortic flow velocity
EMS	Electromechanical systolic
R-R mask	Expected R-R interval trend
R-R mean	Actual data used
Av rate	R-R rate
Av ctr	No. cardiac cycles used
Efficiency	Ratio--average over total cardiac cycles
Q-wave	Component ECG waveform
T-slope	Time to peak Z slope
TZ max	Time to peak Z
DZA	Time to diastolic peak
TZ rise	Time to PEP to DZ max
TZ fall	Time from max to DZX

include the measurement of identical parameters in the female population. The transducer-to-anatomy interface on female subjects poses a unique set of design problems, as indicated in the user design criteria. Further problems are reducing user resistance and enhanced wearability. Figures 11 and 12 illustrate an STI electrode configuration for a female subject wherein comfort and natural anatomy-to-transducers interface is accomplished with a brassiere and a choker necklace. To the left in Figure 12 is a male shirt collar with STI electrodes built in. Figures 13 and 14 illustrate the incorporation of IPPM devices within shoewear for both male and female populations, as a means of including these systems in a natural way without sacrifice of scientific data. (Note that both male and female measurements must be identical in support of valid statistics.) In both users, comfort and interface play a major role in valid physiologic data acquisition. In both the shirt collar and choker necklace, an infrared bolometer transducer is incorporated to monitor thermal blood flow rate; i.e., multimode transducers or an illustration of transphysioware.

Finally, in the design of IPPM systems, every possible avenue of incorporating systems into clothing, headwear, shoes, belts, and jewelry must be considered in light of the need of portable, humanly compatible IPPM systems design.

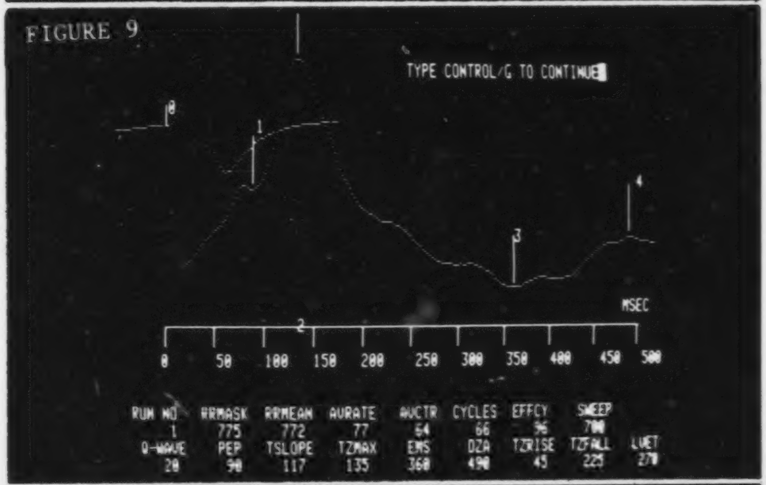
FIGURE 8


225
200
175
150
125
100
75
50
HEART RATE
85%
SECONDS
0
30
60
90
120
150
180

```
REAL-TIME EXERCISE DATA TO DISK

ADVANCE TO NEXT STAGE
TERMINATE TREADMILL EXERCISE-
```

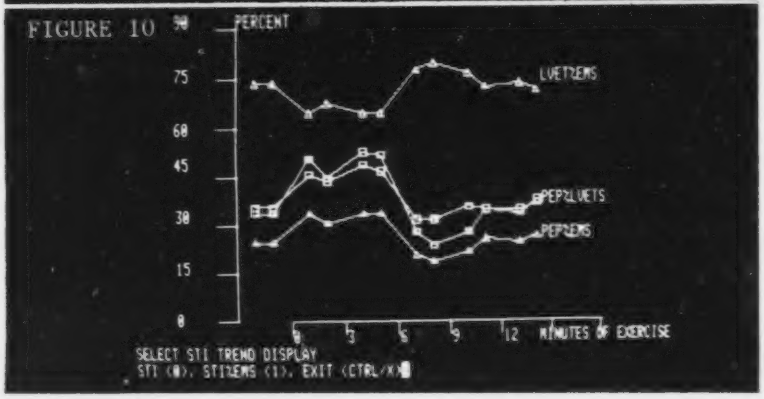
FIGURE 9


0
1
2
3
4
MSEC
0
50
100
150
200
250
300
350
400
450
500

```
TYPE CONTROL/G TO CONTINUE

RUN NO  RRMASK  RRMEAN  AVRATE  AVCTR  CYCLES  EFFCY  SWEEP
     1     775     772      77     64      66     96    700
Q-WAVE     PEP  TSLOPE   TZMAX    EMS     DZA TZRISE TZFALL  LVET
    20      90     117     135    360     490     45    225   270
```

FIGURE 10


90
75
60
45
30
15
0
PERCENT
LVET%EMS
PEP%LVETS
PEP%EMS
0
3
5
9
12
MINUTES OF EXERCISE

```
SELECT STI TREND DISPLAY
STI (0), STI%EMS (1), EXIT (CTRL/X)
```

FIGURE 8. Real time display exercise ECG heart rate trend display during "Bruce" exercise protocol. Highly applicable for IPPM and medical-legal safety. FIGURE 9. Aortic impedance cardiogram after processing by 8010 microcomputer. Note: parameters, bottom of display. FIGURE 10. Trend display of impedance cardiograph parameters. Highly applicable to IPPM systems as a data base generator.

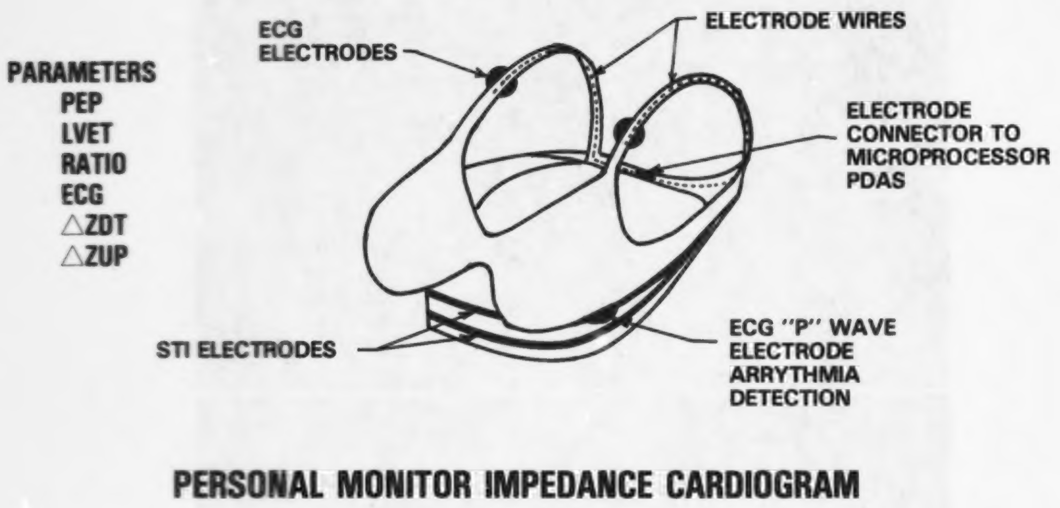

PARAMETERS
PEP
LVET
RATIO
ECG
△ZDT
△ZUP
ECG ELECTRODES
ELECTRODE WIRES
ELECTRODE CONNECTOR TO MICROPROCESSOR PDAS
STI ELECTRODES
ECG "P" WAVE ELECTRODE ARRYTHMIA DETECTION
PERSONAL MONITOR IMPEDANCE CARDIOGRAM

FIGURE 11. Cardiac impedance transducer-to-anatomy interface. Statistical data base requires identical measurements on male and female subjects.

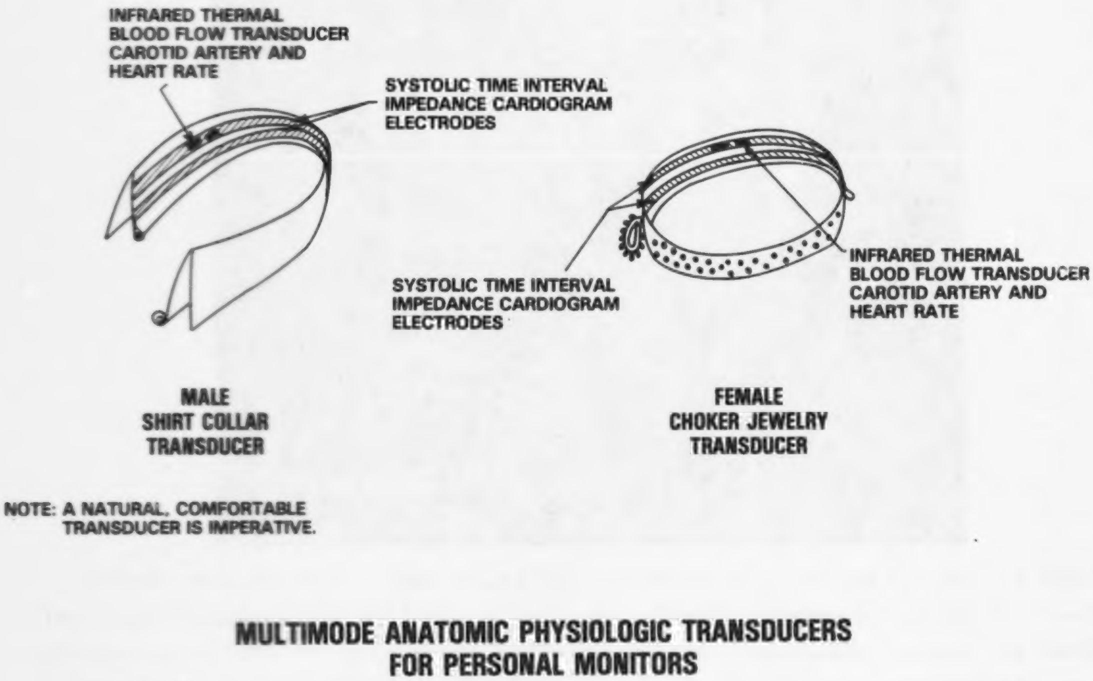
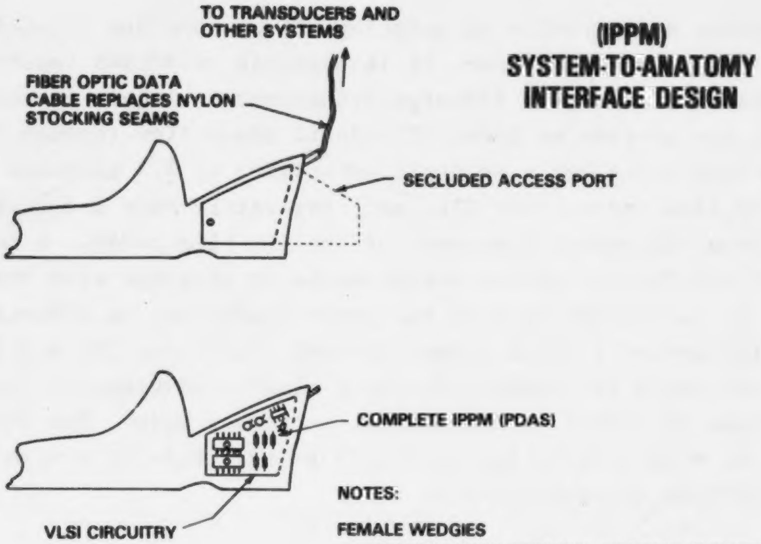

INFRARED THERMAL BLOOD FLOW TRANSDUCER CAROTID ARTERY AND HEART RATE
SYSTOLIC TIME INTERVAL IMPEDANCE CARDIOGRAM ELECTRODES
SYSTOLIC TIME INTERVAL IMPEDANCE CARDIOGRAM ELECTRODES
INFRARED THERMAL BLOOD FLOW TRANSDUCER CAROTID ARTERY AND HEART RATE
MALE SHIRT COLLAR TRANSDUCER
FEMALE CHOKER JEWELRY TRANSDUCER
NOTE: A NATURAL, COMFORTABLE TRANSDUCER IS IMPERATIVE.
MULTIMODE ANATOMIC PHYSIOLOGIC TRANSDUCERS FOR PERSONAL MONITORS

FIGURE 12. Cardiac impedance transducer incorporated into normal dress wear; i.e., reduction of user resistance.

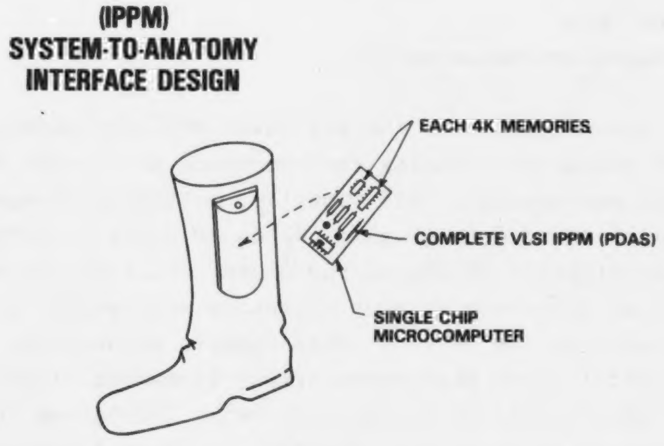

(IPPM)
SYSTEM-TO-ANATOMY
INTERFACE DESIGN
TO TRANSDUCERS AND
OTHER SYSTEMS
FIBER OPTIC DATA
CABLE REPLACES NYLON
STOCKING SEAMS
SECLUDED ACCESS PORT
COMPLETE IPPM (PDAS)
VLSI CIRCUITRY

NOTES:

FEMALE WEDGIES

1. SHOCK PROOF PERSONAL MONITOR VLSI CIRCUITRY.
2. COMFORTABLE, EASE OF USE, AND ACCEPTANCE BY SUBJECT.
3. DOES NOT INTERFERE WITH DAILY TASKS WHILE COLLECTING DATA.
4. FIBER OPTIC CABLES REPLACE STOCKING SEAMS AS DATA LINKS TO OTHER SYSTEMS.

FIGURE 13. IPPM devices must be incorporated within natural human attire.


(IPPM)
SYSTEM-TO-ANATOMY
INTERFACE DESIGN
EACH 4K MEMORIES
COMPLETE VLSI IPPM (PDAS)
SINGLE CHIP
MICROCOMPUTER

NOTES:

MALE WORK BOOT

1. HEAVY BOOT. HAS IPPM MODULE AS OUTBOARD SYSTEM.
2. IPPM IN LEFT BOOT, POWER PACK IN RIGHT BOOT. USES FIBER OPTIC DATA AND POWER LINKS BETWEEN BOOTS THROUGH CLOTHING SEAMS.
3. IPPM MODULE RETURNED BY MAIL FOR MAINTENANCE. FIELD REPLACEMENTS AT MODULAR LEVEL.

FIGURE 14. IPPM system for construction worker.

With software modification of existing STI systems and retaining the common STI electrode configuration, it is possible to record respiratory rate. Additionally, adding an infrared transducer or liquid crystal to the neck electrode may provide an index of carotid blood flow through I-R thermal radiation of blood which has a spectral emissivity at 9.3 microns. Hence, infra-red blood flow index, ECG, STI, and respiratory rate measurements are all feasible from the common placement of the STI electrodes. A further enhancement of respiratory volume measurements is possible with impedance pneumography, if calibrated against the pneumotachograph as illustrated in the construction worker's tidal volume system. Combining STI and tidal volume measurements could be accomplished on a single individual through dedicated IPT systems operating in a multimicroprocessor mode. The data array made possible by this combination is listed below. This is a more specific example of multimode transphysioware.

Cardiopulmonary Parameters
Respiratory rate
Respiratory volume
Respiratory flow
Respiratory tidal volume
Heart rate
ECG
I-R blood flow rate
All STI and impedance measurements.

It should be noted again that the STI Intel 8010 microcomputer is serving as an intelligence converter reducing the abundance of cardiac data into a meaningful clinical measurement. Additionally, multimode parameters are displayed in the form of trend data (Figure 10) as an index of subtle response. The stand-alone capabilities of the microcomputer (4,11,15,17) permit direct support to a clinical data base without extensive statistical support of large ADP systems such as the UNIVAC. This example illustrates the cost effectiveness of "intelligent microcomputerized biomedical instruments" (IMBI). With 64K single chip microcomputers being introduced in 1979 (15), the complete STI system software and ensemble averaging illustrated above could be packaged (less graphics display) within the subject's belt, shoes, or hat. With the abundance of high-density memory, nitrate metal oxide field effects (NMOST), long-term memory storage (1 to 10 years) is also feasible. NMOST memories could be interrogated in post-data collection analysis to review graphics and trends for the generation of an urban data base. Extension of this design philosophy is the basis of IPPM, IPT, multimode transducers, and multimicrocomputer systems. Furthermore, this design philosophy is expandable to include future designs adaptable to changing protocols (through changing software, not hardware) within internal and external IPPM devices presently beyond the state-of-the-art as of this writing. Additionally, the design concepts presented here could well be the forerunners of future internal and external IPPM and IPT 3 to 5 years hence.

CLINICAL VALIDATION OF EPIDEMIOLOGIC PROTOCOLS IN PERSONAL MONITOR DESIGN

Any new approach such as IPPM noninvasive physiologic measurement always contains a question as to the efficacy of the parameter under analysis. The clinical validation of IPPM systems advocated here are based on the use of the EPA Clinical Environmental Laboratory (CEL) as an "IPPM test center" for the evaluation and validation of all personal monitors. The efficacy of all IPPM and dosimeter designs would be dynamically exercised under physiologic and pollutant performance conditions prior to use in any epidemiologic urban health effects program (13). As such, the CEL provides a unique controlled clinical setting sufficient for semi-invasive and external physiologic data acquisition system investigations.

Once preliminary IPPM systems become available, pilot studies in both air pollutant and physiologic data acquisition may be conducted and evaluated against known clinical and air chemistry standards. Use of the CEL as a "national standards resource" for design, development, and evaluation of IPPM would provide a common data base for the design of such systems. Further, the CEL facilities would provide a basis for validating clinical and pollutant dosimetry protocols advocated in IPPM systems prior to field epidemiologic studies. Hence, the urban health effects data base would be acquired on a realistic basis. This validation approach is the only method that will ensure a scientifically defensible data base in support of legislation or any public health initiative.

It is advocated here that all IPPM systems would be designed and developed in this context, wherein the clinical and environmental standards of the CEL would serve as the EPA national standard resource for those interested in certification of such systems and devices.

CONCLUSION

The advocacy of new personal monitor designs has been presented through implementation of microcomputer technology and interactive protocols. Incorporating clinical rationale and judgment within software algorithms at the clinical level has been demonstrated through design examples. Extending this technique to the personal monitor level in population studies remains to be implemented. However, with the acceleration of high-level VLSI technology, microcomputers, and submicron systems in the immediate future, the attainment of a clinical environmental preventive medicine data base as an urban early-warning system is a realistic possibility. Conversely, if epidemiologic research retains present methodologies, the results may continue at present levels of knowledge.

A major thrust in the design and development of IPPM and IPT devices is imperative if useful epidemiologic health effects data is desired. Developments of this type must be designed to maximize clinical flexibility in terms of changing environmental needs, assessment of new pollutant episodes, and adaptability to new research protocols. A significant barrier presently exists in terms of adequately designed physiologic/anatomic transducers which are compatible with male and female subjects. Subject comfort and ease of use are paramount if physiologic data are to be collected in their natural state. The concepts proposed here advocate a new design approach in physiologic transducers and systems which must be incorporated within clothing, shoewear, headwear, underwear, jewelry, and cosmetics. Additionally, transducers must function at an intelligent level through microcomputer software as a means of reducing size, weight, and power while improving comfort and clinical utility.

Finally, it is envisioned that any design initiated today must be flexible enough to be adaptive and useful to new protocols 2 to 3 years later, when priorities will most certainly change. It is, therefore, the responsibility of systems designers and program managers to invest in appropriate research and development efforts in the implementation of IPPM systems in response to an effective public health initiative. Part II of this paper addresses future needs through anticipatory research.

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Discussion

CHAPMAN: Robert Chapman, EPA. Matt, I got a little confused. In the middle of your talk, you showed a system on a male in which he had three ECG leads on, and he had a couple of straps around his chest, and he also had some straps around his neck. And then two slides later you showed a picture of a shirt collar with some things in it. Would this now be part of the same system, or are we sort of jumping ahead to an even smaller system?

PETROVICK: No. This system requires two sets of electrodes--a pair on the neck and a pair at the thoracic cage. The slide with the shirt collar only indicated how that electrode could be packaged so it would be functional and aesthetically pleasing. The other electrodes would be contained under the shirt. So, there are four electrodes, and you seclude them in clothing and such.

Design of Personal Monitors for External and Internal Physiologic Studies in Health Effects (Part II)

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INTRODUCTION

Scientific assessment of urban health decrements resulting from air pollutant exposures has eluded clinical investigators to the extent that a definitive urban health effects data base remains a high priority in support of EPA legislation. More importantly, a definitive urban clinical data base would provide a means for establishing early-warning guidelines in preventive environmental medicine as a public health initiative. However, the need for an early-warning data base has not been uniformly recognized in terms of epidemiologic research, due to the obvious lack of properly designed transducers, clinical instrumentation, and logistic resources.

The key significance of an urban early-warning data base is predicated on the ability to characterize dose-response relationships at a highly individualized level through personal monitoring. Systems which are capable of accurately documenting both physiologic and air pollutant variables simultaneously are essentially nonexistent. It is, therefore, incumbent upon clinical and environmental scientists to systematically assess the urban epidemiologic needs toward the design, development, and implementation of personal monitors capable of simultaneous physiologic and air pollutant data acquisition.

Such a system, Healthe-Belt, was advocated by Petrovick et al. in 1974 (7). It was the opinion of several peer groups (in 1974) that technology could not support a personalized pollutant and physiologic data acquisition system design. It is still common to hear various researchers suggest the improbability of detecting dose-response variance in normal mobile adults resulting from pollutant exposures. Unfortunately, such assessments of personal monitors are speculative and not based on credible scientific investigation. Conversely, the latter rationale is reasonable and consistent with antiquated clinical technology. Today, new technology (10,12,13) further confirms the Healthe-Belt concept in that through appropriate research and development, such a goal is entirely feasible. Specifically, the explosive advances (10) in microcircuitry, submicron components, very large scale integration (VLSI), microprocessors, and microcomputers can be implemented and configured for simultaneous pollutant dosimetry and physiologic data acquisition systems. In view of the accelerated pace of VLSI technology and the need for constantly changing health effects protocols, it is imperative to design personal monitors (PM) with maximum flexibility toward adaptation to changing clinical needs.

Part I of this two-part report sets forth design guidelines and criteria for personal monitors using today's technology. This report is intended to set forth an entirely new philosophy 3 to 5 years beyond that advocated in Part I, as a means of personal monitor design that is adaptable to and anticipates changing clinical, epidemiologic needs. Accordingly, a research rationale must be developed such that any R&D of PM attempted must anticipate clinical needs and advances of modern technology in order to effectively respond to the urban epidemiologic needs.

The following fundamentals are therefore proffered, somewhat specifically in the area of clinical physiology and high-level technology as supportive resources to a public health initiative capable of characterizing urban health effects resulting from air pollutants. As such, these fundamentals may be used as basic research guidelines in the design and development of internal and external intelligent personal physiologic monitors (IPPM) in search of new knowledge.

FUNDAMENTAL BASIC RESEARCH RATIONALE

It is imperative to:

1) Increase new knowledge and understanding of external and internal physiology in order to avoid present-day limitations in parameters, transducers, techniques, and technology.

2) Conduct exploratory studies in the search of new physiologic parameters specific to assessment of urban health effects.

3) Conduct exploratory research in wearable external and internal IPPM devices.

4) Conduct exploratory studies in the design and development of new transducers, systems, and devices to permit assessment of internal and external physiology as a basis for increasing new knowledge from which to draw upon in the development of new parameters.

5) Apply the knowledge of existing and future technology--such as very large scale integration, microcircuitry, microcomputer techniques, software engineering, intelligent transducers, and interactive clinical judgment--as a means of developing new methodologies specific to urban epidemiologic assessment of health effects research.

6) Support an in-depth, comprehensive budget structure that is responsive to cost effectiveness and long-term research support for the design and development of new tools for this endeavor.

Implementation of the above rationale has considerable potential for the evolution of several new physiologic parameters, transducers, and techniques as basic research spinoffs. This potential can be realized in terms of productive research that is "made to happen" by departure from traditional technology and clinical techniques.

PHILOSOPHY OF INTERNAL AND EXTERNAL PHYSIOLOGIC MONITORS

The test subject transducer criteria (Part I) impose a significant problem in the physical packaging of IPPM systems design. Use of multimode transducers will require the basic analog sensors, electrodes, etc., followed by a level of intelligent signal processing, artifact screening, rejection, and simplification of data in response to call from higher-order multiprocessor systems. Incorporation of these features can only be accomplished through a revolutionary change in technology, such as implementation of micro- and submicron-component technology in IPPM design.

In the search for new physiologic parameters and techniques to supplement conventional physiologic data acquisition systems (PDAS) measurements, a new design initiative is imperative to overcome the extreme limitations of conventional noninvasive clinical research. The development of new techniques must permit feasibility studies for design and development of new systems.

Feasibility prototypes must be investigated, constructed, and clinically validated before use in epidemiologic studies.

Noninvasive physiologic parameters have predominantly been associated with some form of interfacing transducers to the external anatomy (8,12). Few, if any, options exist for internal physiologic measurement, or it seems that way in the sense of classic design rationale. However, properly designed systems at the internal level may serve as prototypes for future external physiologic data acquisition systems. The latter is the basis of internal exploratory research via IPPM PDAS designs described in this paper.

Physical size and available real estate (on-board the subject) for transducers cannot in all cases be based on discrete component (TTL) logic, in view of bulk, power, and physical encumbrances to the subject. However, it is feasible to perform many discrete circuit functions, such as signal processing, with software rather than hardware logic; i.e., a first-derivative amplifier function can be accomplished with an algorithm corresponding to a low-pass (hardware) filter function. Logic process control functions can well be performed with software logic, thus eliminating the need for TTL circuit logic devices without loss of basic function. Essentially, transducers designed to incorporate software as a process function become uniquely compatible in microcomputer-controlled personal monitors. It is immediately recognized that software rather than hardware logic will require considerable memory in each IPPM. However, with VLSI technology today, 64K microcomputer memory modules (10) in a 40 pin dip package can easily accommodate transducer functions, as well as most interactive protocols and emulated circuit logic. Herein is the key significance of microcomputer technology. Transducers incorporating microprocessors integral to their function may serve as IPPM system peripherals in a multiprocessor mode (8,10). Each transducer could communicate through an I/O port as a direct memory-addressable DMA peripheral. This approach would free the bus master to operate on higher-level priority functions, while system interrupts from peripherals would be initiated only when relevant subtle changes occur. Incorporation of microcomputers, microprocessors, and peripheral devices into transducers and IPPM systems cannot be accomplished effectively unless a quantum jump (8,9,10) in component size and high-density packaging is attained within industry. Furthermore, test subject space is needed for air dosimetry sensors and devices on the same test subject to ensure simultaneous PDAS and air pollutant assessment. The VLSI techniques definitely are a move in the proper direction. However, the design of IPPM external and internal systems advocates a combination of VLSI and submicron component technology based on standardized modularized subsystems.

To illustrate the design principles and problems advocated in IPPM systems, several design examples are proffered as initial design concepts.

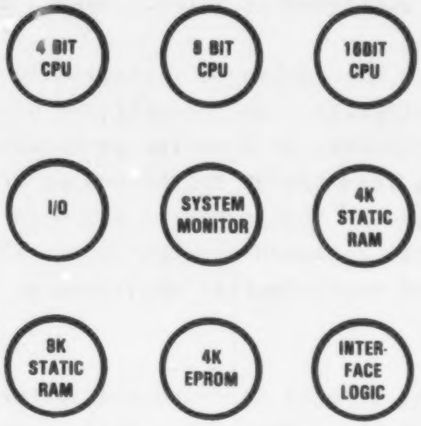
Design of IPPM systems requires a high degree of anticipation of clinical need (8) prior to the principal investigator's own recognition of a given need. As such, maximum software flexibility to changing protocols with minimal hardware changes is a significant requirement in the design of IPPM devices. The design philosophy expounded in this paper is based on today's needs with tomorrow's technology. This approach ensures design flexibility, cost effectiveness, and elimination of technological obsolescence at the completion of a given design.

It is immediately recognized that several hardware and software devices advocated here are not currently available. Therefore, these designs are considered to be design goals and examples that should be attained in response to urban epidemiologic needs. It is further recognized that availability of such devices are possible, and that these designs can be made to happen if a realistic public health initiative is advocated and supported. Designs initiated at the present time will require a lead time of 18 months to 3 years, based on the acceleration of VLSI technology today. Hence, it behooves program managers and designers to plan urban epidemiologic health programs with these factors well in mind. The need for micro- and submicron technology (8,10) in intelligent physiologic monitors is of significance in that urban health effects personal monitoring cannot be successfully accomplished without this resource.

ILLUSTRATIVE DESIGN

VLSI and Submicron Technology

With the packing density of VLSI, and with submicron technology increasing and the physical size decreasing, standardized subsystems such as 8-16 bit microprocessors, I/O devices, static RAM, ROM, tri-state buffers 8, 16, 32, 64K memories, and system controllers could be manufactured as precanned, modularized system wafers. Additionally, selection of individualized microcomputers at the 4 to 16 bit level could be designed quickly and simply if precanned hardware and software were available in modular wafer form. (See Figure 1.) Modularized subsystems would be used as if they were discrete (TTL) components, and IPPM designing would be accomplished at systems level by utilizing prevalidated systems and software protocols. This design capability would provide significant clinical flexibility in adapting any system modules to individualized IPPM systems.

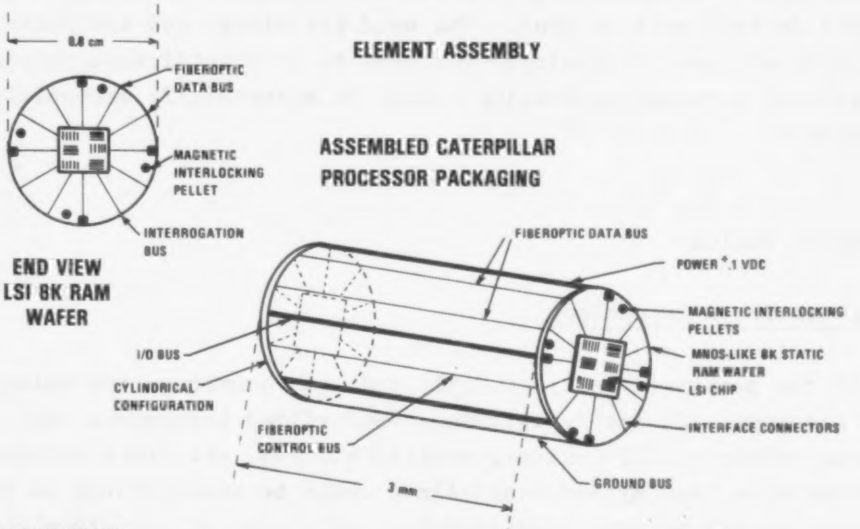

4 BIT CPU
8 BIT CPU
16BIT CPU
I/O
SYSTEM MONITOR
4K STATIC RAM
8K STATIC RAM
4K EPROM
INTER-FACE LOGIC

1. PHYSICIANS PRESCRIPTION DEFINES THE PROTOCOL AND PARAMETERS OF MEASUREMENTS.
2. SOFTWARE ENGINEERING ANALYZES REQUIREMENTS, DRAWS ON STANDARDIZED ALGORITHMS FOR BIO-MEDICAL MEASUREMENTS.
3. SYSTEMS ENGINEERING FILLS PRESCRIPTION THROUGH ASSEMBLY TO MEET PHYSICIANS NEEDS.
4. Q-A BIOLOGICAL SAFETY CHECKS PERFORMED.
5. DELIVER TO CLINIC.
6. PHYSICIAN ADMINISTERS TO PATIENT.
7. UPON RETRIVAL, DATA INTERROGATION PROCESS FEEDS RESULTS INTO DATA RESPONSE BANK.
8. PHYSICIAN REVIEWS RESULTS, ADMINISTERS FURTHER HEALTH CARE MANAGEMENT OF PATIENT. RELEASE FROM HOSPITAL.

NOTE:

1. INDUSTRY STANDARDIZED WAFER SUBSYSTEMS – PRESCRIPTION COMPONENTS.
2. PRESCRIPTION DESIGN BY PHYSICIAN AT A BLOCK DIAGRAM LEVEL. COMPONENTS USED AS IN DISCRETE COMPONENT CIRCUIT DESIGN.

FIGURE 1. Modular wafer subsystem components used as discrete systems rather than the classic TTL logic approach.


0.8 cm
ELEMENT ASSEMBLY
FIBEROPTIC DATA BUS
MAGNETIC INTERLOCKING PELLET
INTERROGATION BUS
END VIEW LSI 8K RAM WAFER
ASSEMBLED CATERPILLAR PROCESSOR PACKAGING
FIBEROPTIC DATA BUS
POWER ±.1 VDC
MAGNETIC INTERLOCKING PELLETS
MNOS-LIKE 8K STATIC RAM WAFER
LSI CHIP
INTERFACE CONNECTORS
I/O BUS
CYLINDRICAL CONFIGURATION
FIBEROPTIC CONTROL BUS
GROUND BUS
3 mm

NOTES:

1. ALL I/O DATA BUS CONTROL BASED ON TIME SHARED FIBEROPTIC BUS STRUCTURE.
2. SINGLE WAFER ELEMENTS SNAP TOGETHER MAGNETICALLY. PERMITS STACKING AND SYSTEM ASSEMBLY BY SEGMENTS TO MATCH PHYSICAL CONFIGURATION DESIRED.
3. ALL WAFERS ARE MEMBERS OF A STANDARDIZED STRUCTURE PERMITTING BLOCK DIAGRAM DESIGN.
4. ALL MAJOR ELEMENT SYSTEM WAFERS TO BE USED AS IF THEY WERE DISCRETE COMPONENTS, i.e., RESISTORS/CAPICITORS.

ADAPTIVE CATERPILLAR PROCESSOR PACKAGING

FIGURE 2. System wafer modules high density packaging for internal/external physiologic exploration.

Ideally, microprocessors used with IPPM should take the form of standardized devices (8,9,10) with specific capabilities in a physical configuration, thus ensuring maximum flexibility to individually designed systems. Additionally, the mechanical and electronic packaging should be in a form which enhances all power, I/O data bus, control bus, and interface connections (Figure 2). The physical shape of modules used in any system should be easily adaptable to individual subject configurations, thus enhancing ease of assembly by semitechnical personnel.

Figure 2 illustrates an example of two adaptive wafer designs that snap together in serial fashion. This packaging scheme would permit various shapes, curvatures, or caterpillar-like segmented designs as an example. Ideally, several wafer modules could be assembled to suit a particular study protocol for urban health effects screening. Both pollutant dosimeters and PDAS systems could be designed by this process so as to ensure miniaturized systems compatible with personal mobility.

Finally, the physical hardware should be designed at a modular level such as a wafer configuration. Each module would serve as a subsystem such as MCPU, I/O, RAM, ROM, and interface devices. This would permit the physician to prescribe a system design at a block diagram level, thus avoiding unnecessary design detail. The physician would select his/her design based on a diagnostic data base matrix (8) (see Figure 3), and the protocol he/she feels is most beneficial in a specific urban epidemiological study. Designing an IPPM with pretested, modularized systems would eliminate the use of time-consuming discrete components, connections, and hardware debugging, while ensuring standardization of selected protocols.

Clinically, the physician's physical examination and diagnosis of the subject is at a physiologic-systems level, including, for example, judgments on the EEG, blood pressure, blood chemistries, etc. Why not, then, tailor the IPPM to follow a similar analytic rationale in collecting physiologic data and provide for a total systems approach to health effects research. Hence, upon completion of preliminary studies, the physician could write a prescription to design an external IPPM to suit a specific protocol for a selected population group and related pollutant (which is a form of prescription engineering). The protocol would ensure exact measurements to be made by previously proven algorithms which, in the final analysis, provides the physician with data useful in the final data base. Semitechnical personnel would construct the IPPM in accordance with the prescription, and they would return it to the physician to administer to the population group.

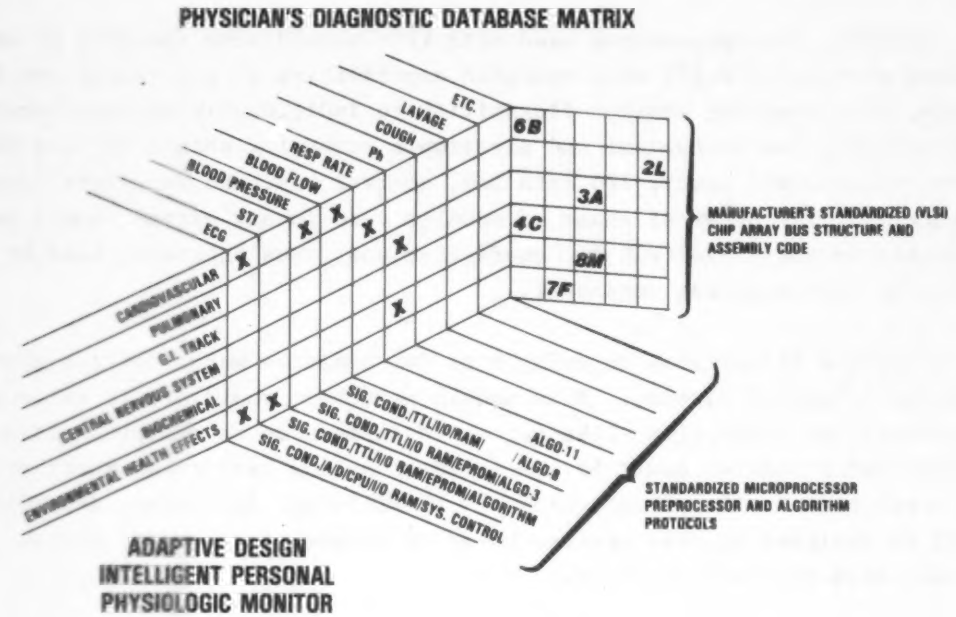

PHYSICIAN'S DIAGNOSTIC DATABASE MATRIX
ETC.
LAVAGE
COUGH
Ph
RESP RATE
BLOOD FLOW
BLOOD PRESSURE
STI
ECG
CARDIOVASCULAR
PULMONARY
G.I. TRACK
CENTRAL NERVOUS SYSTEM
BIOCHEMICAL
ENVIRONMENTAL HEALTH EFFECTS
X
6B
2L
3A
4C
8M
7F
MANUFACTURER'S STANDARDIZED (VLSI) CHIP ARRAY BUS STRUCTURE AND ASSEMBLY CODE
SIG. COND./TTL/I/O/RAM/ ALGO-11
SIG. COND./TTL/I/O RAM/EPROM/ ALGO-8
SIG. COND./TTL/I/O RAM/EPROM/ALGO-3
SIG. COND./A/D/CPU/I/O RAM/SYS. CONTROL ALGORITHM
STANDARDIZED MICROPROCESSOR PREPROCESSOR AND ALGORITHM PROTOCOLS
ADAPTIVE DESIGN
INTELLIGENT PERSONAL
PHYSIOLOGIC MONITOR

FIGURE 3. This matrix is used to rationalize an IPPM design configuration in a short period of time by utilizing proven protocols and systems. This approach is much more responsive in assessment of pollutant episodes.

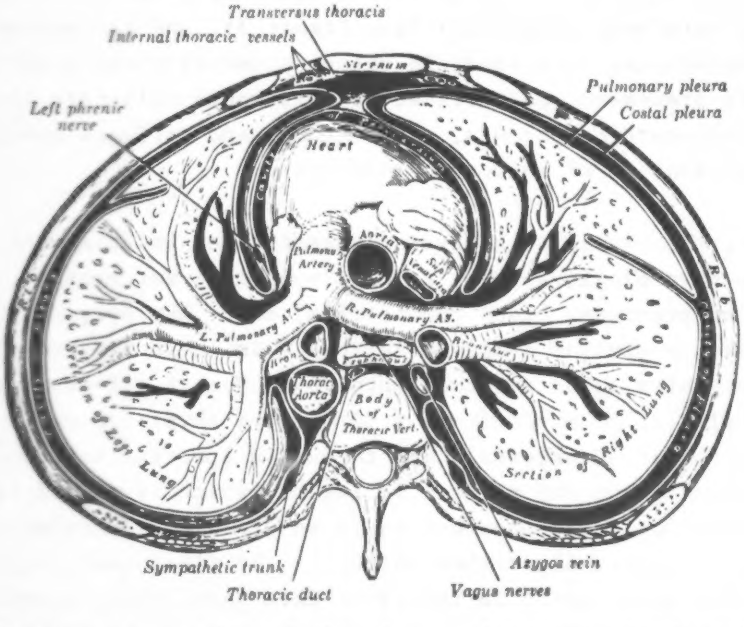

Transversus thoracis
Internal thoracic vessels
Sternum
Pulmonary pleura
Costal pleura
Left phrenic nerve
Heart
Aorta
Pulmonary Artery
Sup. Vena cava
L. Pulmonary A.
R. Pulmonary A.
Bron.
Oesophagus
Thorac Aorta
Body of Thoracic Vert.
Section of Left Lung
Section of Right Lung
Rib
Sympathetic trunk
Thoracic duct
Azygos vein
Vagus nerves

FIGURE 4. Transverse section of the thorax showing anatomic relationship of the esophagus to heart and lungs.

In the search and exploration for new physiologic parameters and transducers, semi-invasive (internal) studies hold potential for the development of new measurements and techniques for use in IPPM external systems through new knowledge and techniques. However, suitable transducers and subsystems do not presently exist on the shelf to permit such investigations, and, therefore, must be specifically designed. The design of IPPM systems thus advocates individualized systems which permit the charting and characterization of limited internal physiologic function. Hence, a whole new philosophy in the acquisition of external and internal physiologic data must precede the design of IPPM's.

INTERNAL IPPM PDAS

Clinical gastrointestinology (1) has in the last two decades developed a wide variety of techniques for swallowable instrumentation devices in the form of ECG electrodes, temperature sensors, pressure transducers, telemetry systems, and balloon-mounted devices, each representing discrete components. To this date, there has been little effort toward the design of coordinated internal multiparameter systems. Gastroenterology techniques, however, have previously demonstrated that a number of physiologic parameters can be measured internally from the esophagus through and to the GI tract. Figure 4 illustrates an anatomic transverse section of the thorax relative to the heart, lungs, and the esophagus or survey site for semi-invasive IPPM for use in clinical exploration. Table 1 illustrates an example of parameters detectable internally by the designs proposed herein.

The semi-invasive parameters available for clinical study and evaluation in the design of IPPM systems provide a significant potential for a cardiopulmonary data base. Initially, the study of these parameters must be performed under careful clinical management, such as in the "Clinical Environmental Laboratory" or CEL (Strong 1978) (11). The major impasse, however, is the lack of properly designed IPPM systems for internal data acquisition.

Utilizing the principles of the PDBM and VLSI technology, a brief illustration of internal IPPM systems design is presented as follows.

EXPLORATORY INTERNAL PHYSIOLOGIC DATA ACQUISITION SYSTEM

Utilizing the IPPM wafer systems modules developed from the PDBM, a 500-mg envelope (Figure 5) is instrumented with two inflatable elastomer

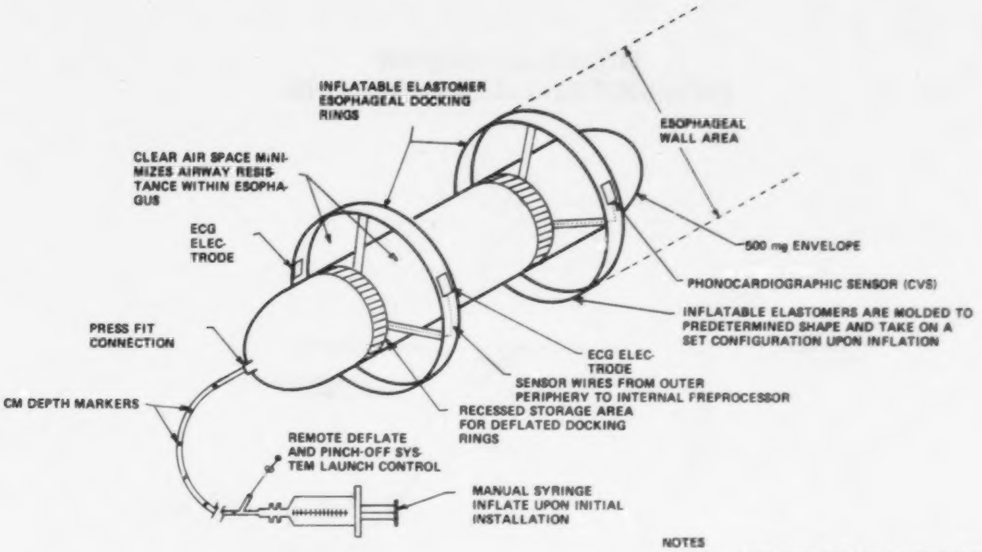
TABLE 1

Physiologic Parameters Detectable from Internal Esophageal PDAS

Respiratory rate
Respiratory volume
Respiratory tidal volume
Cough rate and intensity
Heart rate stress--medical-legal safety
ECG "P" wave arrhythmia detection
Heart sounds--cardiac valves
Temperature
pH
Echocardiogram
New parameters

docking rings, as a means of fixing and stabilizing the IPPM within the esophagus at the level of the cardiac orifice (Figure 6). Each docking ring contains a pair of transducers--one pair for pulmonary and one pair for cardiac measurements. Measurement of respiratory volume, rate, and tidal volume are all feasible from the piezoelectric (6) transducers $({}^{P}Z_{t})$ located within the inflatable docking rings located in the esophagus. Clinically, a flexible tube (track) similar to an esophageal balloon leader is inserted through the nasal-pharyngeal cavity until it is visible orally at the posterior pharyngeal wall of the mouth. The IPPM is contained within a 500-milligram envelope and is attached through the mouth to the flexible track and then passed down the track or to the monitoring site of interest. Once located anatomically, the physician inflates the elastomer docking rings with the syringe, thus placing the pulmonary and ECG transducers against the inner walls of the esophagus at the level of the cardiac orifice or posterior of the heart. Functionally, the piezoelectric transducers $({}^{P}Z_{t})$ are used in a multimode transphysioware, wherein one transducer performs the initial anatomic interface, and a software algorithm performs multiparameter acquisition of cardiac parameters.

The piezoelectric (6) transducer lends itself to a wide variety of physiologic measurements, such as low- and high-frequency pressure, and acoustic sensing. It is well known that shunting a specifically cut piezoelectric sensor with external resistance or capacitance can dramatically change the


INFLATABLE ELASTOMER ESOPHAGEAL DOCKING RINGS
ESOPHAGEAL WALL AREA
CLEAR AIR SPACE MINIMIZES AIRWAY RESISTANCE WITHIN ESOPHAGUS
ECG ELECTRODE
500 mg ENVELOPE
PHONOCARDIOGRAPHIC SENSOR (CVS)
INFLATABLE ELASTOMERS ARE MOLDED TO PREDETERMINED SHAPE AND TAKE ON A SET CONFIGURATION UPON INFLATION
PRESS FIT CONNECTION
ECG ELECTRODE
SENSOR WIRES FROM OUTER PERIPHERY TO INTERNAL FREPROCESSOR
CM DEPTH MARKERS
RECESSED STORAGE AREA FOR DEFLATED DOCKING RINGS
REMOTE DEFLATE AND PINCH-OFF SYSTEM LAUNCH CONTROL
MANUAL SYRINGE INFLATE UPON INITIAL INSTALLATION

NOTES

1. ANATOMIC LOCATION AT CARDIAC ORIFICE TO DETECT ECG AND HEART SOUNDS, i.e., "P" WAVE DETECTION ARRYTHMIA PROCESSING, MYOCARDIAL INFARCT.
2. UPON COLLECTION OF CARDIAC DATA, THE SYSTEM IS REMOTELY LAUNCHED BY THE INVESTIGATOR BY DEFLATING THE CAPSULE AND THE BREAKAWAY PNEUMATIC TUBE.
3. UPON SYSTEM LAUNCH, THE CAPSULE TRAVERSES ITS ROUTE THROUGH THE G.I. TRACT COLLECTING VARIOUS PHYSIOLOGIC DATA.
4. VALIDATION STUDIES TO BE CONDUCTED IN LABORATORY ANIMALS.

**INTERNAL EXPLORATORY SYSTEM
FOR PHYSIOLOGIC DATA ACQUISITION**

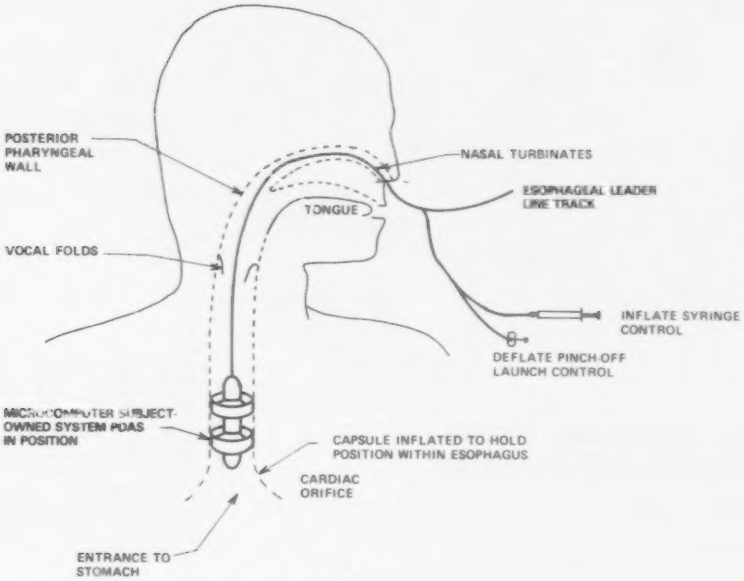
FIGURE 5. This device is supportive to basic physiology in the search for new parameters and transducers.

characteristics of the ${}^{P}Z_{t}$ element. Changes in "Q," the equivalent circuit merit, and the frequency response can cause the ${}^{P}Z_{t}$ sensor to readily respond to and detect DC to high-frequency information.

As a considered design approach, one could attain multimode functions through remote tuning of a piezoelectric transducer with a software algorithm. In this design, the objective is to remotely change the ${}^{P}Z_{t}$ characteristics within the swallowable microcomputer, upon software command, to sense the following parameters:

- Gastric motility
- Gastric pH
- Cough rate and intensity
- Respiratory rate
- Heart sounds
- ECG "P" wave-arrhythmias
- Heart rate.

INTERNAL EXPLORATORY
PHYSIOLOGIC DATA ACQUISITION SYSTEM


POSTERIOR PHARYNGEAL WALL
NASAL TURBINATES
ESOPHAGEAL LEADER LINE TRACK
TONGUE
VOCAL FOLDS
INFLATE SYRINGE CONTROL
DEFLATE PINCH-OFF LAUNCH CONTROL
MICROCOMPUTER SUBJECT-OWNED SYSTEM PDAS IN POSITION
CAPSULE INFLATED TO HOLD POSITION WITHIN ESOPHAGUS
CARDIAC ORIFICE
ENTRANCE TO STOMACH

NOTE:

1. SYSTEM INSTALLATION SIMILAR TO SWALLOWING ESOPHAGEAL BALLOON.
2. CAPSULE IS ATTACHED TO THE LEADER LINE TRACK AFTER PASSAGE THROUGH NASAL PHARYNGEAL WALL.
3. PHYSICAL ATTACHMENT THROUGH ORAL CAVITY AT POSTERIOR PHARYNGEAL WALL AREA.
4. APPROPRIATE ANESTHETIC IS USED TO DESENSITIZE GAG REFLEX – A NORMAL PROCEDURE.
5. AFTER THE SYSTEM IS INFLATED AND INSTALLED, THE LEADER LINE TRACK, SYRINGE, AND PHYSICIAN'S LAUNCH CONTROL IS REMOVED.
6. THE LAUNCH CONTROL REMOVAL PINCHES THE PNEUMATIC LINE SO AS TO PROVIDE A SLOW LEAK ALLOWING SPECIFIC TIME BEFORE LAUNCHING INTO THE STOMACH.

FIGURE 6. Internal PDAS is an investigative tool in support of external IPPM.

Conceptually, the $^{P}Z_t$ is interfaced to a specifically addressed input port of the microcomputer device. A controlling algorithm applies a limited voltage to a tri-state buffer-like and ladder network device. By this process, the $^{P}Z_t$ is remotely tuned through a common MOST/FET-like voltage-controlled resistor which changes the "Q" of the $^{P}Z_t$ for the measurement of a specific physiologic parameter. This design advocates the use of one $^{P}Z_t$ sensor which acts as a peripheral device containing a specific input port address. Access of this input port to the control bus is through a form of tri-state buffer. Each of the above parameters may be detected by a change of shunting impedance to the ${}^{P}Z_{t}$, thus altering the low/high frequency-response to detect the above parameters. This process is repeated in sequence to perform the above measurements from internal firmware. Each sequence algorithm, of course, identifies in memory the sensor mode, parameter, data, and subject ownership while in use. Figure 7 illustrates how the same IPPM microcomputer can through prevalidated (EPROM)-like algorithms, remotely tune or change ${}^{P}Z_{t}$ characteristics for use in pulmonary rate and volume measurements.

By this process, it may be feasible to detect two or more physiologic measurements from a single transducer (multimode). The related algorithm, of course, would preprocess these signals into meaningful clinical measurements--i.e., transphysioware. Another option is to retrieve data from long-term memory (1 to 10 years), such as is possible with the new metal-nitrate-oxide silicone transistor (MNOST) semiconductor memories within a given IPPM. Data interrogation of the IPPM by high-level computer would permit a form of data base development in the off-line mode through interactive graphic analysis, as illustrated in Part I.

In another mode, the platinum electrodes on the 500-milligram PDAS, (Figure 5) can detect heart rate and "P" wave arrhythmia through associated clinical rationale in the form of a prevalidated algorithm designed for this purpose. A further mode time shares the platinum electrodes for measurement of esophageal pH or gastric pH if the IPPM is inserted beyond the cardiac orifice and into the root of the stomach. If the IPPM is located at the cardiac orifice, respiratory rate, cough rate, and cough intensity are also possible to detect. The acoustic cough signal would be converted through software (RMS signal processing) to a DC voltage and compared with the diaphragmatic pressure recoil during a cough. If both signals occurred simultaneously, a software logic algorithm would verify the cough rate, intensity, and duration (as opposed to artifact). This would be of particular value in exercise pulmonary ozone exposure studies, in which frequently there is a coughing response after 4 hours of ozone at .6 ppm.

MYOCARDIAL CONTRACTILITY OF CARDIAC PUMP FUNCTION

Taking full advantage of semi-invasive internal IPPM, it is feasible to perform "cardiac impedance systolic time interval" (2,3,4,5) measurements

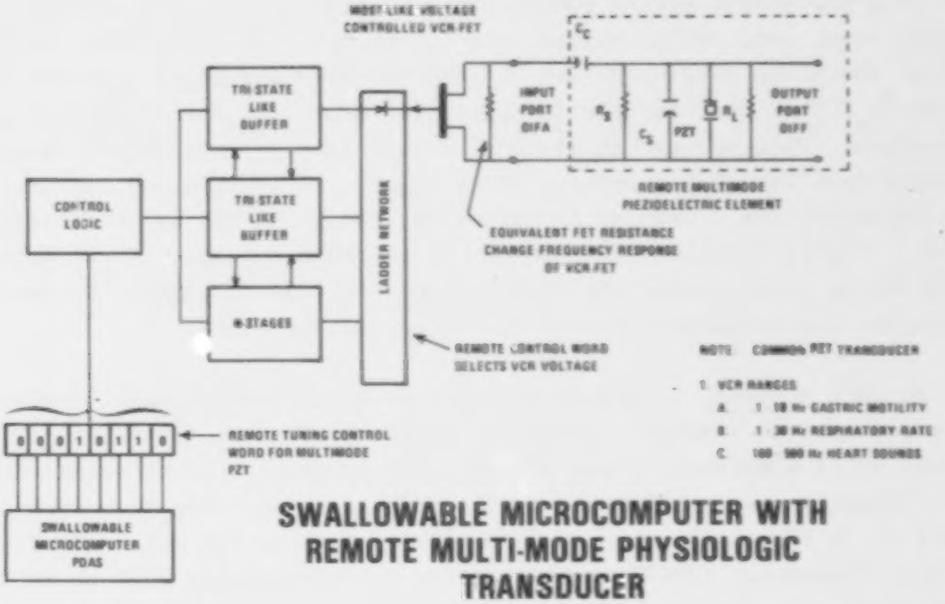

MOST-LIKE VOLTAGE
CONTROLLED VCR-FET
TRI-STATE LIKE BUFFER
TRI-STATE LIKE BUFFER
N-STAGES
CONTROL LOGIC
LADDER NETWORK
C_C
INPUT PORT DIFA
R_S
C_S
PZT
R_L
OUTPUT PORT DIFF
REMOTE MULTIMODE
PIEZOELECTRIC ELEMENT
EQUIVALENT FET RESISTANCE
CHANGE FREQUENCY RESPONSE
OF VCR-FET
REMOTE CONTROL WORD
SELECTS VCR VOLTAGE
NOTE: COMMON PZT TRANSDUCER
1. VCR RANGES
A. 1 - 10 Hz GASTRIC MOTILITY
B. 1 - 30 Hz RESPIRATORY RATE
C. 100 - 500 Hz HEART SOUNDS
0 0 0 1 0 1 1 0
REMOTE TUNING CONTROL
WORD FOR MULTIMODE
PZT
SWALLOWABLE
MICROCOMPUTER
PDAS
SWALLOWABLE MICROCOMPUTER WITH
REMOTE MULTI-MODE PHYSIOLOGIC
TRANSDUCER

FIGURE 7. When space constraints exist, and multiple parameters are desired, this concept can be very effective.

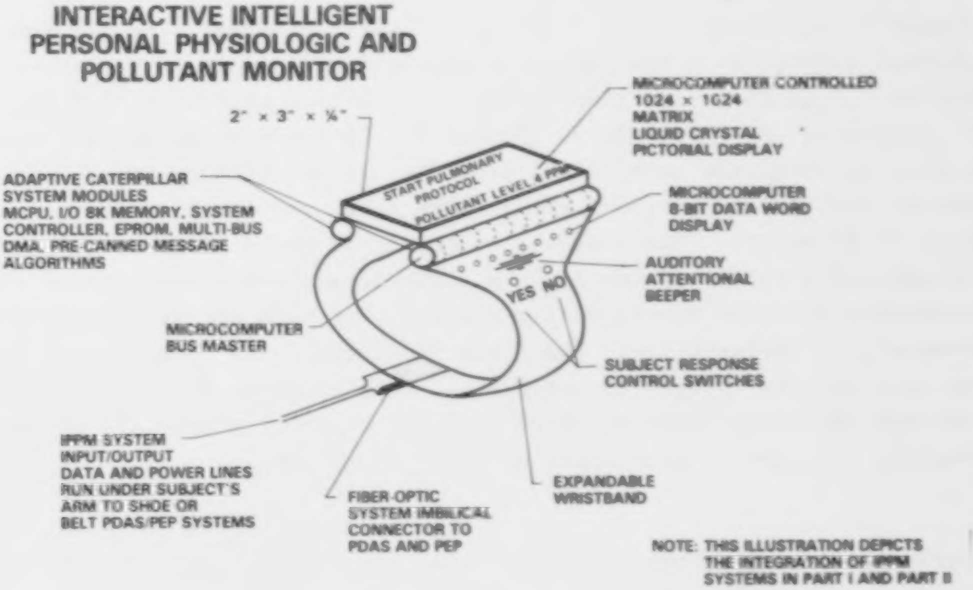

INTERACTIVE INTELLIGENT
PERSONAL PHYSIOLOGIC AND
POLLUTANT MONITOR
2" × 3" × ¼"
MICROCOMPUTER CONTROLLED
1024 × 1024
MATRIX
LIQUID CRYSTAL
PICTORIAL DISPLAY
START PULMONARY
PROTOCOL
POLLUTANT LEVEL 4 PPM
ADAPTIVE CATERPILLAR
SYSTEM MODULES
MCPU, I/O 8K MEMORY, SYSTEM
CONTROLLER, EPROM, MULTI-BUS
DMA, PRE-CANNED MESSAGE
ALGORITHMS
MICROCOMPUTER
8-BIT DATA WORD
DISPLAY
AUDITORY
ATTENTIONAL
BEEPER
YES
NO
MICROCOMPUTER
BUS MASTER
SUBJECT RESPONSE
CONTROL SWITCHES
IPPM SYSTEM
INPUT/OUTPUT
DATA AND POWER LINES
RUN UNDER SUBJECT'S
ARM TO SHOE OR
BELT PDAS/PEP SYSTEMS
FIBER-OPTIC
SYSTEM IMBILICAL
CONNECTOR TO
PDAS AND PEP
EXPANDABLE
WRISTBAND
NOTE: THIS ILLUSTRATION DEPICTS
THE INTEGRATION OF IPPM
SYSTEMS IN PART I AND PART II

FIGURE 8. IPPM display provides means of implementing systematic field protocols in the absence of supervisory clinical personnel. Pretraining of subjects is required.

as an index of myocardial contractility. Impedance STI measurements permit an array of cardiac performance measurements similar to those reported in Part I. However, if an internal IPPM system for this purpose is desired, the system design would require a specific configuration as follows: a conventional esophageal balloon is instrumented to include two foil electrodes around its inner surface, while two additional electrodes are placed around the subject's neck at the carotid artery level. The neck electrodes are excited with a 100-KHz carrier signal, while the esophageal balloon electrodes are positioned near the cardiac orifice or the level of the aortic root of the heart.

As each cardiac cycle occurs, the electrical impedance carrier signal is modulated by the aortic flow velocity (first derivitive impedance) at the aortic root level, and an analog impedance signal is detected. Each cardiac cycle is preprocessed by ensemble averaging and stored in memory. If immediate STI data is sought, signals are passed out through the nasal pharyngeal cavity by fiber optic data lines to an external microcomputer. This process would permit real time exercise analysis of STI, as illustrated in Part I. If it is desired to collect and store periodic internal STI data for later interrogation and analysis in an off-line fashion, this may be accomplished by storing data in RAM within the IPPM and analyzing them later. The resulting cardiac impedance signals would then be stored in RAM for subsequent analysis after exploratory surveys have been completed. This technique would provide a means of cross-validating the external IPPM/STI device prior to field epidemiologic use.

APPLICATION OF INTERNAL IPPM TO EXTERNAL PHYSIOLOGIC MONITORING

Upon the successful development of the modularized wafer systems (Figures 1 and 2), the packaged systems used for internal exploratory research may also be applied to external personal monitoring.

A critical need in field epidemiologic health effects is the use of the physician's assistant or clinical technician to ensure that field protocol techniques are properly adhered to. Conversely, it is totally impractical to provide clinical technicians with each IPPM during data collection. However, with implementation of microminiaturized visual display screens in the form of a wrist-mounted device (WMD), a form of visual and auditory communication with the trained subject is feasible (as described below).

IPPM WRIST-MOUNTED DISPLAY

The use of liquid crystal pictorial displays (LCPD) have been utilized in recent military aircraft radar systems for target identification and destruction as part of the "Smart Bomb" weapons systems (14). LCPD modules are available as 1-inch-square 100 x 100 visual matrix devices which, through character generator techniques, appear as a postage stamp-sized TV set. Each matrix contains 1,024 x 1,024 digital encoded pictorial elements, which can be electronically stacked to form a 2 x 3-inch visual display (as illustrated in Figure 8). With precanned protocols built into on-board EPROM devices in an IPPM, such a design could be used as a communicative prompting device (STI, Part I) to have the subject follow specific protocol routines without the assistance of a medical technician.

Operationally, the LCPD would have three basic modes of operation, as follows:

- Systems management process controller
- Auditory attentional command and response functions
- Visual prompting and interactive instructions.

SYSTEMS MANAGEMENT PROCESS CONTROLLER (SMPC) MODE

A single microcomputer located in the wrist-mounted device will function as a systems management processor which will control all messages to and from the subject via the LCPD. The SMPC will function as a bus master in a multimicroprocessor environment. One microcomputer will function as a physiologic data acquisition system (PDAS) located in the subject's right shoe (heel) or belt (Part I). A second microcomputer is a pollutant exposure processor (PEP) located in the left shoe (heel) or belt (Part I). Each communicates on-call to the bus master in the wrist-mounted device. The PDAS and PEP systems will function as a multimode bus master/slave system. The bus master will periodically "poll" the PDAS and PEP throughout protocol test periods, thus accessing the two slave systems for relevant subtle response data.

The PDAS and PEP systems will be dedicated as IPPM systems and will contain precanned protocols relative to the detection, processing, and low-level diagnosis and/or interpretation of events. If no subtle effects within the PDAS or PEP systems occur, these systems would report to the bus master only on-call in a routine "polling" mode. However, if a subtle change occurs in either IPPM, either one or both PDAS' or PEP's could interrupt the bus master for "relevancy analysis" by the bus master. In such an event, the bus master will weight out the significance of the physiologic or pollutant effect, and sound an attentional tone to the subject to look at the LCPD for further instructions.

AUDITORY ATTENTIONAL COMMAND FUNCTION (AACF) MODE

Based on a low-level analysis of the PDAS or PEP, the bus master will sound an auditory tone (three beeps) to get the subject's attention. The test subject then responds, acknowledging his/her attention by depressing the "yes" button on the wrist-mounted device.

VISUAL PROMPTING AND INTERACTIVE INSTRUCTIONS (VPII) MODE

Upon test subject attentional response indicating "yes," the bus master is told that the test subject's attention is available for interactive messages in that the subject is viewing the LCPD and awaiting information.

The VPII and LCPD are designed to display precanned messages stored in an on-board EPROM device. An array of interactive prompting messages are called by the bus master and displayed to the subject, depending on the circumstances. In the event of performing specific protocol functions based on previous training in the EPA "CLEANS" facility (i.e., pulmonary function exercise by a construction worker, as in Part I), the subject can be instructed via the LCPD messages and paced throughout a short protocol. As an example:

1) An auditory tone beeps three times and gets the subject's attention.

2) The subject responds by depressing the "yes" button on the WMD.

3) The subject reads the message on the LCPD.

4) The prompting message will instruct the subject to:
    a) Place pneumo in mouth;
    b) Continue rest breathing until 1-minute tone;
    c) Increase exercise until 5-minute tone, then stop.

5) If during the pulmonary exercise protocol the subject's heart rate or other parameter exceeds the maximum level, the PDAS system alarms and interrupts the bus master. The bus master automatically sends three auditory

tone beeps to get the subject's attention. The subject responds with the "yes" button, the bus master replies with the message "STOP"--"STOP," "GO TO REST-STATE." After a period of 1 minute, the bus master polls the PDAS and PEP again. If the subject's heart rate is in excess of prescribed limits, the bus master sends three beeps, and the subject responds with a "yes." The bus master sends the message, "LEAVE WORK AREA"--"SEE PHYSICIAN IMMEDIATELY."

6) If only the PEP alarms without a physiologic response, the bus master sends three beeps, the subject responds with "yes," and the message display indicates "Pollutant Alarm" and continues to flash. A second message is displayed, "LEAVE AREA IMMEDIATELY," and also flashes.

With the combination of protocol-prompting of a trained subject, and low-level diagnosis of PDAS or PEP as an "interactive intelligent personal monitor," IPPM can serve as a low-level adjunct human supervisor in support of and lack of a medical technician of the test subject. Other algorithms and protocols may also access the test subject's own known judgment through prompting messages. This approach permits a joint man-machine interactive rationale as an "intelligent personal monitor" (Part I).

A wide variety of protocols, alarm messages, displays, etc., are feasible through this approach. The functional features of an IPM design of this type are within the state-of-the-art today. However, the submicron technology of microcomputers, with the size and packaging density advocated here, will require considerable research and development. Conversely, devices such as the LCPD currently exist in military fire control systems. The design issue requires access and design integration of a LCPD with an IPM system.

CONCLUSION

The design examples and guidelines for external and internal IPPM systems have been presented through implementation of VLSI, submicron components, and microcomputer technology. Through this process, the concept of the "physician's data base matrix" has been presented as a means of developing the principles of "prescription engineering" in IPPM devices. Prescription engineering provides a key mechanism in the selection of prevalidated protocols and design of adaptive IPPM systems in response to changing research needs, clinical feasibility, cost effectiveness, and the development of an urban clinical data base. The prescription engineering approach to clinical epidemiologic research provides the means of replacing discrete circuit logic with interactive intelligent software logic as a means of reducing physical size, weight, and power. This approach enhances subject acceptance through microminiaturization and elimination of technological obsolescence due to changing health effects mandates.

Prescription engineering by the physician and his or her support team illustrates the principles and problems involved in the interfacing of human anatomy to a physiologic data acquisition system. The anatomic-to-transducer interface is the greatest impasse in IPPM system design, along with concomitant development of new health effects parameters. Further, the importance of common clinical protocols for male and female populations imposes severe but not insurmountable design obstacles. Resolving such design obstacles is illustrated by design examples in Parts I and II through implementation of the concept of multimode transducers. Multimode transducers provide the means of minimal physical transducer placement and maximizing the number of clinically useful parameters. The cardiopulmonary transducers and algorithms proposed here speak to this design philosophy without encumbering the test subject or sacrificing clinical data. This approach also provides the means of using standardized VLSI subsystems and microcomputers, which in quantities needed in clinical epidemiologic research could be more cost effective than any other approach currently available.

Finally, it is fully recognized by the authors that the level of the VLSI technology required in the proposed designs is not currently available. The design concepts presented here have been utilized as building blocks in establishing design principles for the implementation of external/internal IPPM systems in the near future, 3 to 5 years from today. Systems of the type advocated here will not be in the making in the foreseeable future, unless clinical and environmental scientists are enlightened by the potential of new microcomputer technology and apply modern methods to the solution of health care and environmental epidemiologic problems. Conversely, we must recognize that microcomputers are not "cure all" devices and that their implementation must be based on a balanced engineering approach. If we fail to adopt the design principles similar to those defined in Parts I and II, the lack of a realistic, simultaneous air dosimetry and physiologic data acquisition system will continue to stagnate environmental science. A new strategy for the design of personal physiologic monitors is required as a means of implementing a public health initiative. The philosophy of internal semi-invasive data acquisition systems is introduced as a means of conducting exploratory physiologic research in support of this strategy. Through this approach, it is anticipated that a new prospective will spawn new knowledge, parameters, and techniques that may be extrapolated to external intelligent personal physiologic monitors.

It is abundantly clear that through technology of today and in the next 5 years, simultaneous pollutant and physiologic personal monitors shall be implemented through the design philosophies and principles presented in Parts I and II. The issue is not how, but when, will clinical and environmental researchers put forth the necessary research and development effort to bring IPPM systems into being. Again, it is fully recognized that several concepts and devices advocated here do not presently exist; they must be made to happen, as was done in exploration of the moon. For this reason, appropriate design goals presented here must be established. The internal/external approach to IPPM systems represents the ultimate design. Critics will scoff and allude to such innovations as being products of technological intoxication. However, we need only look back at the progress of personal monitor design in the last 5 years to realize that personal pollutant and physiologic monitors were advocated in 1974 Healthe-Belt, but still do not exist today; hence, a loss of 5 years that could have better served the public.

A significant problem in epidemiologic urban health effects data acquisition is lack of supervisory clinical technicians to administer the protocol as in the EPA "CLEANS" facility. The liquid crystal pictorial display device is not a complete solution to the problem. However, such a system could serve as an interim solution to the field logistics of urban epidemiology.

These proposed concepts and design philosophies will in all probability meet with similar pessimism, as in the past, without the benefit of scientific research. In considering the explosive technology of today and the next 5 years, the design cycle time for an external IPPM is 18 to 24 months. This period of time must be followed by appropriate clinical validation studies for an additional year. Once such a system is clinically accepted for field epidemiologic use, a minimum of a 2-year field study would be required. Hence, the design-to-data-base cycle time would not be unusual at 5 years. The key question is: can an urban public health initiative afford to wait another 5 years (a total of 10 years) before appropriate R&D support is implemented to provide a supportive legislative health effects data base?

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Personal Cardiopulmonary Electrode Monitoring

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Research Triangle Park, North Carolina

Environmental health effect studies are usually designed to correlate controlled pollutant dose with health effect decrement. In the experimental laboratory, accurate dose measurements are compared to standard cardiopulmonary parameters. Typical physiological measurements include respiratory rate, respiratory volume, alveolar-arterial oxygen gradient, heart rate, and electrocardiogram stress response (30). While such experiments provide useful and reproducible information, they could be supplanted with studies involving subjects performing their normal daily routine by employing personal exposure and physiological data monitors.

The initial target organ for airborne pollutants is the lung, and, consequently, respiratory function measurements are commonly examined. Adverse pulmonary function may affect oxygen transport with resulting changes in cardiac performance, especially under increased workloads. As heart and lung disease are prominent in our society, a significant subpopulation is sensitized and susceptible to adverse cardiopulmonary effects. Although pollutants which permeate the pulmonary membrane may be transported to all organ and tissue systems, it is unlikely that such health effects could be studied with personal monitors.

Cardiopulmonary measurements are, therefore, the most promising choice for personal monitor health effect studies; however, the selection of suitable noninvasive cardiopulmonary measurement techniques is limited. The necessary physiological data must be acquired with ease, comfort, and accuracy in order to gain favor with both the investigator and subject volunteer.

Using only surface electrodes, the electrocardiogram (ECG) is routinely used for monitoring changes in heart rate, rhythm, and muscle physiology. A second electrode technique, thoracic electrical impedance (TEI) measurement, is an experimental method which detects changes in cardiac muscle performance and pulmonary physiology. Together, the ECG and TEI provide a comprehensive assessment of cardiopulmonary function and physiology which appears well suited for personal monitoring and environmental health effects research.

ELECTROCARDIOGRAM

The physiology and measurement of the ECG are well known and routine in modern clinical practice (7,12). Contraction and excitation of cardiac muscle are accompanied by tissue currents which give rise to millivolt potential differences at the body surface. The normal ECG presents a rhythmic waveform pattern which is fairly reproducible among different subjects with the same electrode placement. Changes in the waveform may occur with drug therapy, exercise, cardiac ischemia, and other physiological inputs.

Although the ECG electrode placement may vary, three-lead differential amplifier input is generally used to provide high common-mode noise rejection. The V5 precordical lead measures the ECG close to the heart, yields a large amplitude with minimal motion artifacts, and is often used in exercise studies (Figure 1). The primary electrode is placed on the midclavicular line over the fifth intercostal space, the reference electrode above the sternum and the indifferent electrode on the lower right thorax.

In the apparently healthy individual, the ECG is primarily used for heart rate measurement. Since systemic oxygen delivery is determined by cardiac output (stroke volume * heart rate), the heart rate is a factor in determining the cardiac response to a given workload. Maximal stroke volume is roughly attained at 40 percent of the individual maximal oxygen uptake (1, 14), and the remaining work response is accommodated by increasing heart rate alone.

THORACIC ELECTRICAL IMPEDANCE

While the ECG has been studied for nearly a century, TEI measurement is

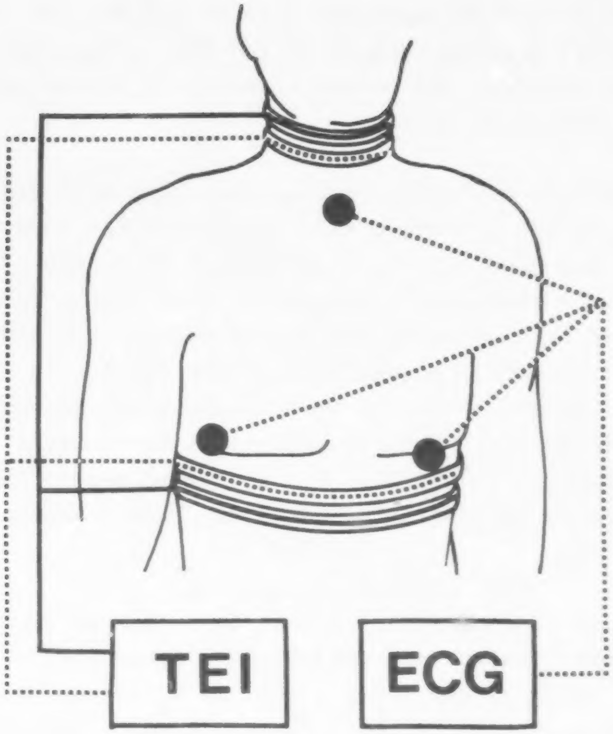


FIGURE 1. Typical configuration for the TEI current source (solid), TEI pickup (dotted), and ECG (dotted) surface electrode interface.

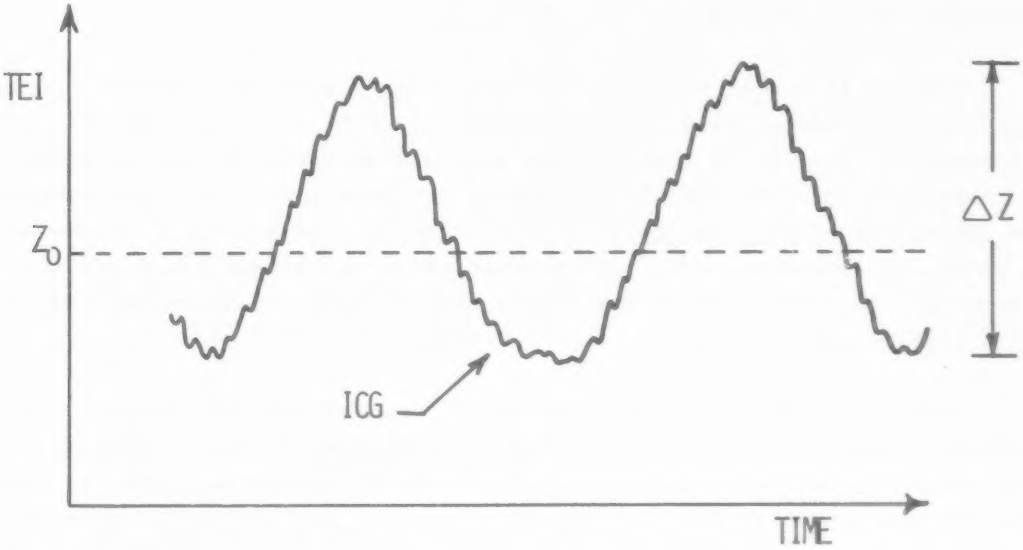


FIGURE 2. Composite sketch of TEI waveform components: mean impedance (Z_o), low frequency respiratory waves (DZ), and high frequency cardiac waves (ICG).

a relatively recent development. First measured in 1932 (2), continued research of the cardiopulmonary impedance effects (27,33) led to NASA instrumentation and clinical studies support (28). The fundamental properties are well reviewed (11); however, the number of recent clinical publications lends itself to further presentation.

A variety of electrode configurations have been reported, and each tends to enhance a specific TEI physiological component. For cardiac and mean thoracic impedance measurement, the four annular electrode system is most popular (Figure 1). A very high frequency carrier signal (4 ma at 100 KHz) is applied to the outer electrodes and passes through the thoracic volume. At the designated frequency, the applied carrier current is completely safe (11). The carrier signal, modulated by intraelectrode volume conduction change, is monitored by the inner electrodes and demodulated to obtain three physiological components (Figure 2). These are the mean or base impedance (Z_o), the low frequency impedance (ΔZ), and the high frequency impedance (ICG) waveforms.

The DC component (Z_o) or mean thoracic impedance is a measure of intrathoracic fluid volume. In animals subjected to acute intravenous hypervolumia and transient saline injections, a fall in Z_o accompanied increases in intrathoracic fluid volume (6,17,31). The noninvasive impedance measurement generally preceded invasive central venous pressure measurement by as much as 45 minutes (6,37). Investigators evaluating Z_o changes in human clinical studies have confirmed that mean thoracic impedance accurately follows the clinical course of pulmonary congestion, edema, and intrathoracic volume overload and forced diuresis (20,38,44,45).

Changes in Z_o can occur rapidly for both healthy and unhealthy individuals, as was demonstrated by a 14-minute treadmill exercise test (5). An increase in circulating blood volume and cardiac stroke volume presented a 3 percent Z_o decrease during the healthy subjects' exercise. The unhealthy subjects, suffering from ischemic heart disease, had a reduced stroke volume reserve and therefore could not accommodate the increased blood volume. Consequently, they had progressive intrathoracic fluid retention, as indicated by a progressive Z_o decrease to a 15 percent total reduction.

Considering the magnitude of these Z_o changes and that patients suffering pulmonary edema may have a 25 percent Z_o reduction, it is encouraging that the normal Z_o may be predicted to 4.5 percent of the actual value by modeling the thoracic geometry (21). Since a decrease in cardiac performance was detectable under exercise stress, changes in Z_o under transient environmental stress might be detected. Furthermore, by computing an expected Z_o value, thoracic fluid accumulation due to chronic exposure may be demonstrated without requiring a 10-year study.

The low frequency TEI waves (ΔZ) due to respiration have been extensively studied (11). The thorax consists of tissues, fluid, and air. Since air is an insulator, the volume of air respired (ΔV) is related to the change in impedance (ΔZ). While the ratio ($\Delta Z/\Delta V$) differs with individual variance in size, thoracic circumference, and subcutaneous fat (18), improved electrodes and individual spirometer or pneumotach calibration allow subsequent continuous respired-volume measurement.

With calibration, ΔZ may be used for monitoring respiratory rate, as is commonly employed for neonatal apnea detection. Regional lung pathology is detectable by comparing ΔZ when each lung is monitored separately. The subject thereby serves as his own control, and, again, calibration is not required (8).

The high frequency TEI waves, synchronous with the cardiac cycle, are the electrical impedance cardiogram (ICG) and the ICG first derivative (DZ/DT) (Figure 3). Over 25 papers and abstracts have been published during 1976-1978 concerning the genesis and application of these waves.

Considerable evidence indicates that the cardiac impedance pulse reflects left and right ventricle ejection into the aorta and pulmonary artery (3,19,35); however, the actual ventricular volume change contributes less than 10 percent of the total impedance change (35). The aortic contribution was predominant in one study (19) and less than 30 percent in another (35). Experiments in a calf with a totally implanted cardiac prosthesis presented an aortic contribution of 60 percent and a pulmonic contribution of 40 percent (3). Clearly, the origin of the high frequency component is complex and unresolved.

A close relation between DZ/DT and aortic blood flow has been observed (28) and verified (43,46). Both the amplitude and time-to-peak derivative of left ventricular pressure (DP/DT) have correlated with their counterpart in DZ/DT (40,41,46). However, in one study, the relation of DZ/DT amplitude to afterload (aortic diastolic pressure) depended upon the experimental intervention (32), which indicates that DZ/DT may be a reliable index of myocardial contractility under controlled conditions (41,42,46).

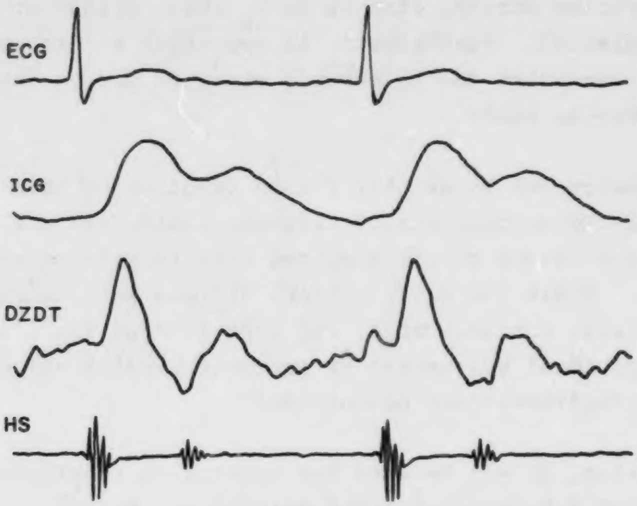
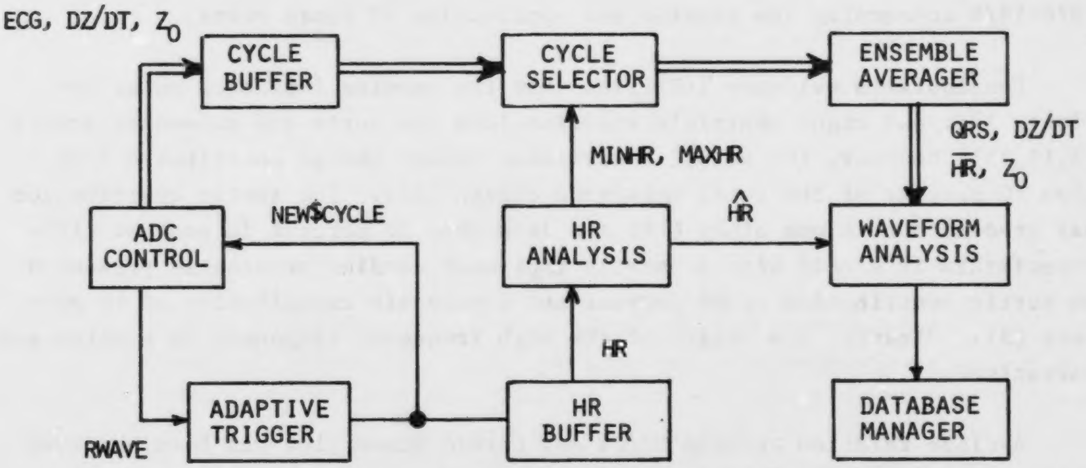


FIGURE 3. Illustration of temporal relationship among the electrocardiogram (ECG), impedance cardiogram (ICG), ICG first derivative (DZ/DT), and heart sounds (HS).


ECG, DZ/DT, Z_0
CYCLE BUFFER
CYCLE SELECTOR
ENSEMBLE AVERAGER
MINHR, MAXHR
QRS, DZ/DT
$\overline{HR}$, Z_0
NEW$CYCLE
ADC CONTROL
HR ANALYSIS
$\hat{HR}$
WAVEFORM ANALYSIS
HR
RWAVE
ADAPTIVE TRIGGER
HR BUFFER
DATABASE MANAGER

SYSTOLIC TIME INTERVAL PROCESSOR

LABORATORY SYSTEM

FIGURE 4. Functional data flow for laboratory systolic time interval processor.

Impedance cardiography has long been a promising method for continuous measurement of stroke volume (27,33). Early studies had resulted in impedance-calculated volumes of higher value than obtained by comparative methods (11). Recent improvements in the impedance model and its application have reduced the differences to within experimental error (9,16,19,26,28,47). Thus, by combining the ECG and TEI, heart rate, stroke volume, and cardiac output are measurable.

The sequence of cardiac mechanical events, collectively called systolic time intervals (STI), correspond to DZ/DT waveform features (29). An automated system for STI measurement using DZ/DT and the heart sounds was first developed in 1974 (22). The excellent correlation of DZ/DT STI features to aortic and carotid STI features is now well established (4,10,15,39). DZ/DT STI measurements have proved reliable in exercise (13,24,36) and postural (42) stress testing as indices of myocardial stress response.

SIGNAL PROCESSING

The necessity for ECG and TEI automated signal processing arises from the complex nature in which the clinical information is contained. Certain waveform features must be identified, interfeature amplitude and time measurements made, and relevant clinical indices computed. As noninvasive methods, both signals are subject to physiological artifacts, transduction artifacts, and uncertainty resulting from their indirect and remote transduction of the physiological source. The TEI is sensitive to a variety of physiological effects which must be isolated prior to measurement. These challenges and their solution have been addressed by analog filter preprocessing, cardiac component ensemble averaging, and waveform feature extraction algorithms (23,24).

The acquisition and analysis of the ECG, Z_o, and DZ/DT signals have been the author's principal interest in this field. Recently, a laboratory-based system for cardiac monitoring during treadmill exercise using these signals was developed under EPA Contract No. 68-02-2772 (25). As an example of the signal processing methods, the ensuing discussion will be limited to the current system design rather than to project-specific processing requirements for a personal monitor.

The EPA Systolic Time Interval Processor (STIP) uses analog signal conditioning prior to digital signal processing and analysis. The ECG is passed through an analog bandpass filter (0.05 to 50.0 Hz) to remove electrode potential baseline shifts and to reduce 60 Hz and high frequency muscle noise. The filtered ECG is passed through a QRS event matching filter (7.2 to 23.4 Hz) to produce the RWAVE event detection signal. The TEI signals (Z_o, ΔZ, DZ/DT) are bandwidth filtered within the commercial impedance instrument and only require amplitude and baseline adjustment.

The ECG, DZ/DT, and RWAVE are sampled at a 400-Hz rate and held in a sample buffer (Figure 4). Each new cardiac cycle is detected by an adaptive trigger algorithm that adjusts the trigger level to the running average RWAVE height. Continuous RWAVE detection is thus assured without manual intervention. With each new cycle, Z_o is sampled and stored with DZ/DT and the ECG QRS complex in a cycle buffer. At the same time, the instantaneous cardiac cycle duration is used to compute and queue the instantaneous heart rate.

When a cardiac function measurement is requested, the remaining processes are activated. In order to further isolate the TEI cardiac component and to improve both the QRS and DZ/DT signal-to-noise ratios, an ensemble of the acquired cycle buffers is averaged. Since the systolic DZ/DT waveform is dependent upon the instantaneous cardiac cycle duration--a natural heart rate variance--premature ventricular contraction or other anomalous ventricular event would invalidate the ensemble average. By selectively averaging cycles of similar duration, these problems are reduced.

To do this, the heart rate buffer is analyzed for the mean expected heart rate (HR), and a 12.5 percent acceptance range (MINHR, MAXHR) is determined. Each successive cycle is compared to these criteria prior to inclusion in the ensemble summation process. The resultant averaged ECG and DZ/DT waveforms are then smoothed and displayed (Figure 5).

The major clinical endpoints for the EPA system are the cardiac systolic time intervals which are relative timing measures between waveform features. Each waveform feature (0, ..., 4) is identified in several stages: 1) the average heart rate is used to estimate the feature waveform segment; 2) the segment waveshape pattern is classified; and 3) the feature is identified using an algorithm based on the pattern classification. A list of quality control parameters and selected clinical indices is then displayed. Finally, the investigation may accept, reject, or flag the cycle for further analysis.

The data base management design has a comprehensive data structure suited

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TYPE CONTROL/C TO CONTINUE
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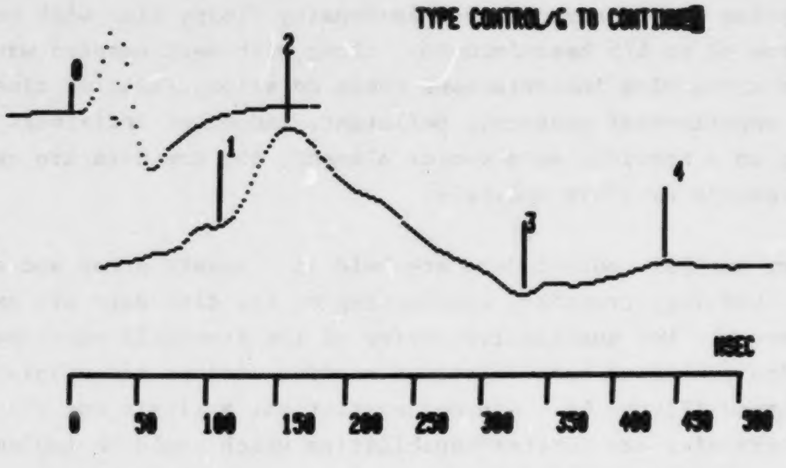

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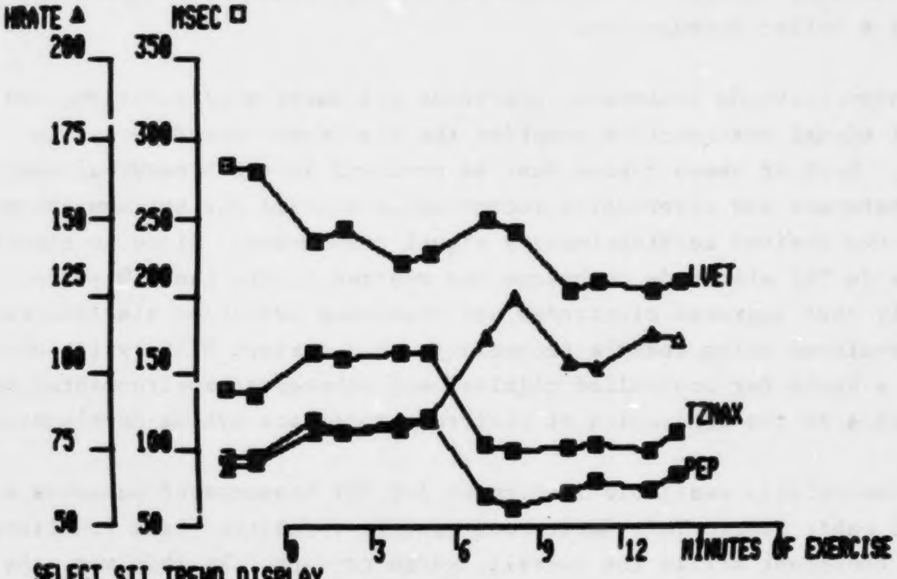
RUN NO.  RRMASK  RRMEAN  AVRATE  AVCTR  CYCLES  EFFCY.  SWEEP
   3      662     662      90     90      90     100     627
Q-WAVE    PEP    TSLOPE  TZMAX   EMG     DZA    TZRISE  TZFALL  LVET
  25      110     135     157    332     440     47      175    222
```

FIGURE 5. Laboratory system graphic display of averaged QRS and DZ/DT waveforms, waveform feature cursors, and resultant data list.



```
SELECT STI TREND DISPLAY
STI (0), STIZEMS (1), EXIT (CTRL/X)
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FIGURE 6. Example trend display of heart rate (HRATE), pre-ejection period (PEP), time-to-peak DZ/DT (TZMAX), and left ventricular ejection time (LVET).

for experimental laboratory analysis. Over a 12-minute acquisition period, 1,570 cardiac cycles may be saved on double-density floppy disc with heart rates ranging from 40 to 175 beats/minute. Along with each sampled waveform is a data vector containing instantaneous cycle duration, relative time, exercise stage, experimental protocol, pollutant, and other individual cycle data. By keying on a specific data vector element, the raw data are easily recalled for automatic waveform analysis.

The waveform analysis output data are held in a memory array and stored on floppy disc. Editing, transfer, and listing of the disc data are executed via the memory array. For qualitative review of the treadmill exercise response, a graphics procedure recalls select cardiac indices and displays their response trend (Figure 6). Grouped statistical analysis and distributed processing data transfer are further capabilities which could be implemented.

PERSONAL CARDIOPULMONARY MONITOR

The EPA STIP laboratory system described in the last section will receive clinical and environmental health effect evaluations during the current year. While a reduction in size and function may be a useful initial approach for a personal monitor design, an expanded outlook for research and development may present a better formulation.

The body-electrode interface, electrode placement configuration, and ECG and TEI signal transduction comprise the electrode interface system (Figure 7). Each of these topics must be reviewed in the biomedical engineering literature and alternative technologies studied for optimum transduction of the desired cardiopulmonary signal components. Since no significant change in TEI electrode technique has emerged in the last 10 years, it is likely that improved electrodes and impedance detection electronics could be developed using today's technology. The current STIP system would be used as a basis for controlled clinical and subsequent environmental health effect studies in the evaluation of electrode interface system developments.

The commercially available instrument for TEI measurement occupies a volume of 1 cubic foot. This instrument must be redesigned as a functional electronic component within the overall system concept. In this way, the electrode interface and control, ECG and TEI transduction, TEI component isolation, analog preprocessing, and digital signal processing could be integrated as a single hybrid microcircuit module. The output data would

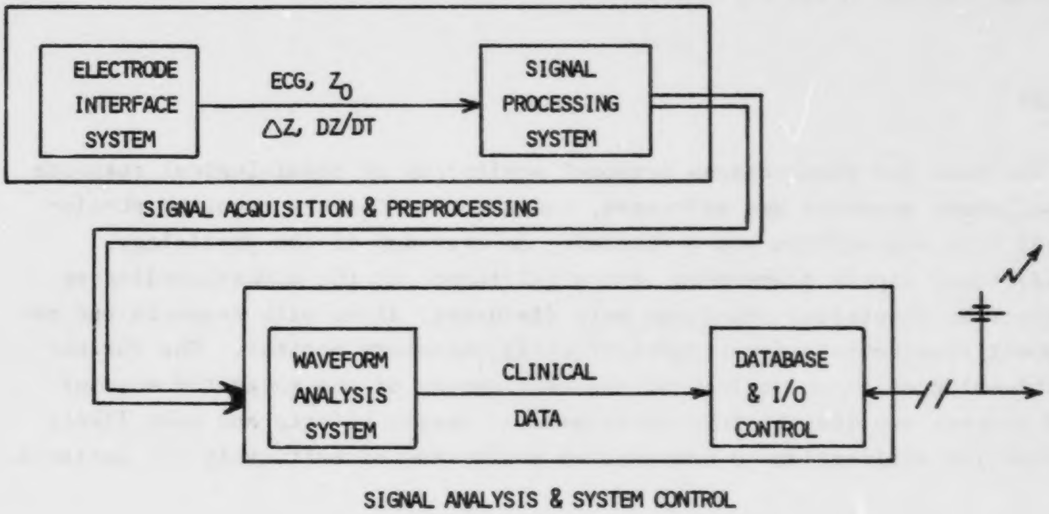
ELECTRODE INTERFACE SYSTEM
ECG, Z_0
ΔZ, DZ/DT
SIGNAL PROCESSING SYSTEM
SIGNAL ACQUISITION & PREPROCESSING
WAVEFORM ANALYSIS SYSTEM
CLINICAL DATA
DATABASE & I/O CONTROL
SIGNAL ANALYSIS & SYSTEM CONTROL

FIGURE 7. Functional diagram of proposed personal cardiopulmonary monitor.

represent analog and digital preprocessed waveform complexes ready for pattern recognition and feature analysis.

Specific physiological waveform processing, data base input/output, and overall system characteristics in communicating with other monitoring devices are general systems engineering problems which require study and formal specification. Current techniques for automated waveform analysis would be reviewed, and--based upon the intended application--appropriate software would be designed. The data base and system functions would be governed by the monitoring application, yet would be designed in a standard format. Implementation of the signal analysis and system control module would rely on standard microcomputer components. As a result, reduction of these system functions from the laboratory system would be straightforward.

The clinical validation is a necessary aspect of any biomedical system development. At the very least, the instrument must operate as specified and record valid physiological measurements. Using controlled environmental response studies and inpatient clinical observations, the cardiopulmonary electrode monitoring concept would be tested. Based on known and expected response patterns, experimental studies would be designed, performed, and evaluated within the environmental laboratory setting. In this manner, the sensitivity, reproducibility, and accuracy of the personal cardiopulmonary electrode monitor would be validated.

SUMMARY

The need for simultaneous personal monitoring of physiological response and pollutant exposure was addressed, and a method for the required physiological data acquisition was presented. An overview of the physiology, transduction, signal processing, and significance of the electrocardiogram and thoracic electrical impedance were discussed, along with research and development requirements for a personal cardiopulmonary monitor. The further investigation of these topics and the development of the suggested monitor would provide new insight into environmental health effects and most likely transfer its application to noninvasive monitoring of critically ill patients.

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Discussion

PETROVICK: Matt Petrovick, EPA. Paul, could you give the group an idea about the practicality of the impedance cardiograph measurements in a roving mobile subject? For example, let's take this scenario: when you get up in the morning, you hop in your car or you walk to work, you get on a bus, you sit down, you go to lunch, and you do all your daily activities, and we would like to record periodically the measurements of systolic time intervals through this process.

How practical do you think this technique is with regard to the severe environment of the artifact from the electrodes? Would you please address that?

KIZAKEVICH: As I have already demonstrated, we have been able repeatedly to monitor patients doing treadmill exercises. In fact, from the work in Miami, we have a paper published in the Heart Journal, December 1978, demonstrating the expected response of systolic time intervals in treadmill exercise through a stage four program. And that is about as severe as you are going to get. You know, that is equivalent to jogging--much faster than jogging down the street. I think there is no problem.

A Respiration-Controlled Personal Monitor

Donald J. Sibbett, Ph.D., and Rudolph H. Moyer, Ph.D.
Geomet, Inc.
Pomona, California

Although a considerable variety of instrumentation such as impingers, cascade impactors, battery-powered air samplers, diffusion collectors, and gas-stain detector tubes is available for applications relating to personal monitoring in industrial and ambient environments, few of the results obtained by such devices are easily relatable to the exposure or dosage of individuals to noxious airborne components. Continuous, electrically powered, and diffusion-controlled collectors fail to measure the varied physiological sampling rates imposed in response to diverse demands for oxygen during a range of activities. Thus, exposure to pollutants during periods of high activity which result in deep and rapid inspiration are weighed equally, in a statistical sense, with periods of shallow breathing, by collection devices utilizing uniform sampling rates. For accurate correlation of exposure with health phenomena, it is highly desirable that air sampling for analytical chemical determinations be proportional to the ventilation rate of individuals under study.

The Geomet Personal Sampler provides a method for sampling air in proportion with the respiration of the wearer. The method is characterized by its use of a carefully designed air pump which is supported next to the diaphragm. The pump is activated by the expansion and contraction of the thoracic cavity during respiration and draws air through a collector which may be varied in accordance with monitoring requirements.

The Geomet respiration-controlled personal monitor consists of five components: 1) the pump, 2) a harness or vest, 3) a sample volume accumulator,

4) a separated digital readout, and 5) a pollutant collector. With the digital readout excepted, the total assembly weighs slightly over 1 pound in its current configuration. The pump and harness weigh 293 g; the battery and accumulator, 207 g; and a typical gas sampler assembly weighs 30 g. A particulate sampling head such as the Bendix Sampling Assembly, Part No. 3900-90, weighs 128 g.

Figure 1 shows the pump, harness, and signal accumulator which are worn during sampling. The pump shown in the center of the picture is made from black ABS plastic. This version, which normally pumps in the 150 to 250 ml/minute range, is 15.5 cm in height, 13 cm wide, and 3.7 cm thick when expanded. Compressed, it is less than 2 cm thick.

The pump housing is connected to a lightweight Velcro harness by three easily connected and adjusted plastic buckles. The harness is passed around the wearer's abdomen and connects to the side ears on the outer pump panel. Over-the-shoulder straps, connected to the circumferential band in the rear, support the inner pump panel at its top. The harness may be adjusted for abdominal measurements up to whatever dimensions are necessary. By use of Velcro tabs, the excess strap is fastened back on itself. Dimensional adjustment of the harness is made at the buckles; the Velcro fastenings are only used to avoid dangling ends.

The pump performance in terms of air displacement is monitored by use of an electronic accumulator which is shown at the right side of Figure 1. This cigarette package-sized instrument contains a 9-volt battery and electronic circuitry to monitor the motion of a linear potentiometer located within the pump housing. The signal from the pot is transmitted through a shielded lead which fastens to one end of the accumulator through a miniature clamped hexagon connector. The accumulator measures and stores potentiometer motion in both directions. The absolute magnitude of this signal is established by screwdriver adjustment of a trim-pot through the package wall. After calibration and adjustment, the accumulator may read out in any desired volume units. As normally calibrated, the readout unit operates in milliliters.

A closer look at the pump is shown in Figure 2. The cross section entitled B on the right shows the extended position of the pump. The pump is returned to this position by the spring, which is shown schematically at the bottom of the figure. All working components are contained within the molded housing and are protected by it from accidental damage.

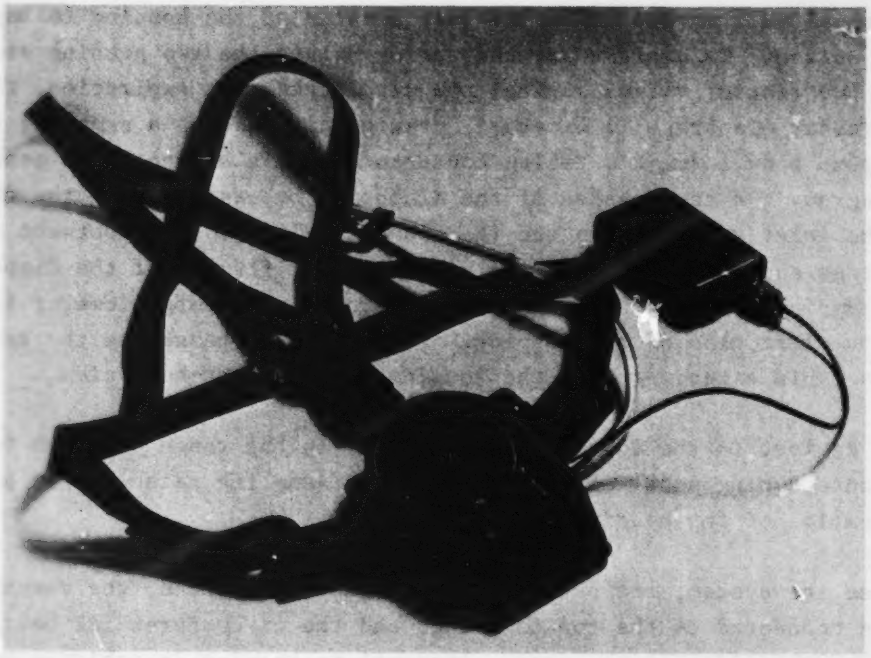

FIGURE 1. The Geomet Personal Monitor. Pump, harness, accumulator, and a typical harness.

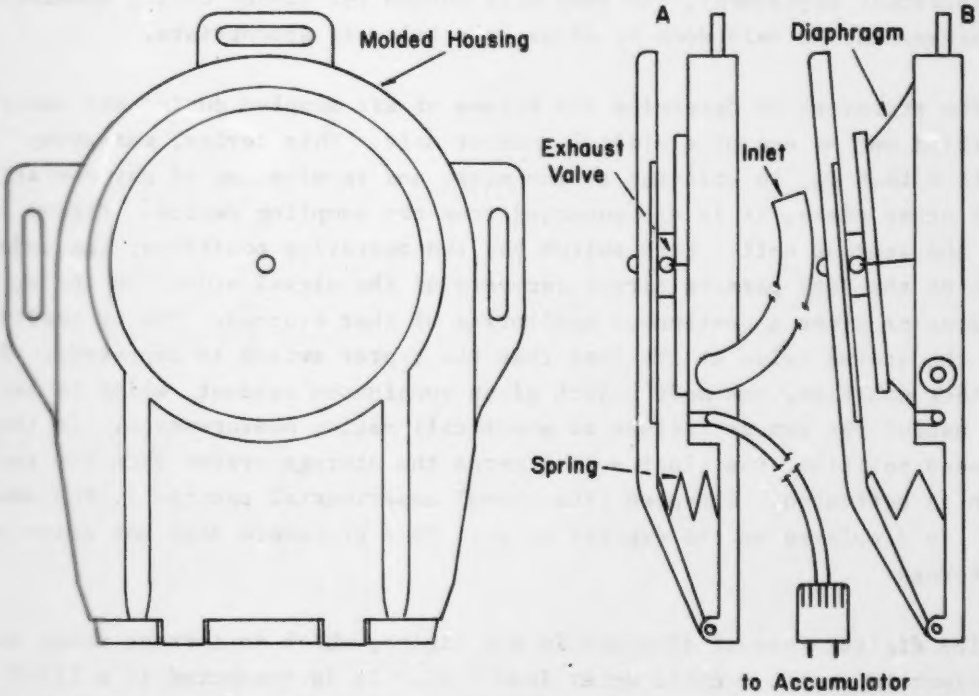
Molded Housing
A
B
Diaphragm
Exhaust Valve
Inlet
Spring
to Accumulator

FIGURE 2. The Geomet Personal Monitor pump.

Abdominal wall motion moves the base section of the housing to impart a pumping motion. On expiration, the spring drives the two housing sections apart and two flapper valves control the air intake. On expiration, the silicone rubber diaphragm is extended, drawing air through a sampling tube into the pump body through a tubing connector visible at the lower center of the diagram. On compression of the diaphragm or expansion of the thoracic cavity, the inlet valve closes and the exhaust valve--located between the rubber diaphragm and the pump cover--opens. Repeated flexing of the diaphragm produces pumping action. The signal-generating linear potentiometer is located on the left side of the housing. The signal is passed to the accumulator by a cable extending from the housing on the right-hand side.

This device, in the described size, pumps in the range from 150 to 250 ml-per-minute during most activities. Changed sampling rates may be achieved by modification of the housing size.

To use the system, the harness is placed over the head, the vee-shaped section is connected to the top coupling, and the circumferential belt is connected to the sides of the pump. Appropriate tension is achieved by pulling the side belting until the pump diaphragm is just slightly compressed during normal exhalation. Harness tension should be barely noticeable. Excessive tightening of the harness will result in poor performance of the pump. With such incorrect adjustment, the pump will bottom (or close) during inhalation. The harness may be held down by clips to a belt, if appropriate.

The procedure to determine the volume of air sampled during any interval is carried out by use of a digital readout unit. This device, measuring 13 x 11 x 16.5 cm, is utilized at the start and termination of any operation. At all other times, it is disconnected from the sampling device. Figure 3 shows the readout unit. Each switch has two operating positions; the mode switch on the left permits direct recovery of the signal stored in the accumulator or gives a continuous monitoring of that storage. The up position gives the stored value at the time that the center switch is depressed. In the other position, the mode switch gives continuous readout, which is basically useful for demonstrations or short-calibration measurements. In the depressed position, the clear switch zeros the storage system when the center switch is activated. Elevated (the normal experimental position), the stored signal is displayed on the digital meter. This procedure does not destroy the storage.

The digital readout displays in six digits, which in current usage is sufficient to sample 1 cubic meter less 1 ml. It is connected to a 115-V

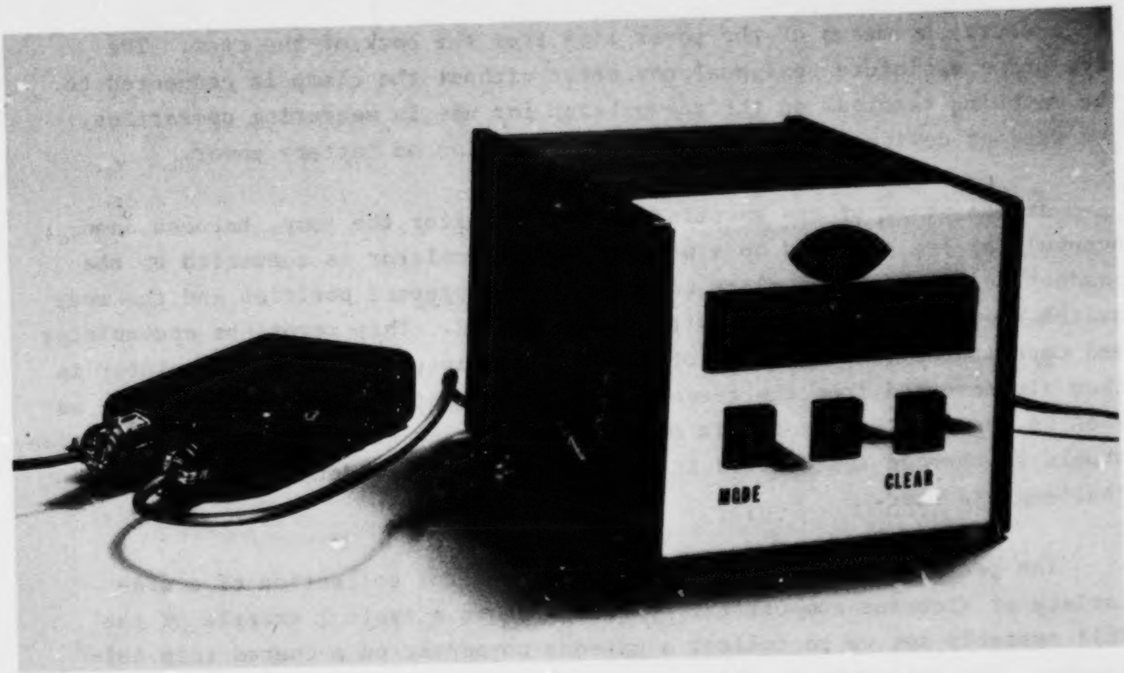

FIGURE 3. Digital readout, connected to electronic accumulator.

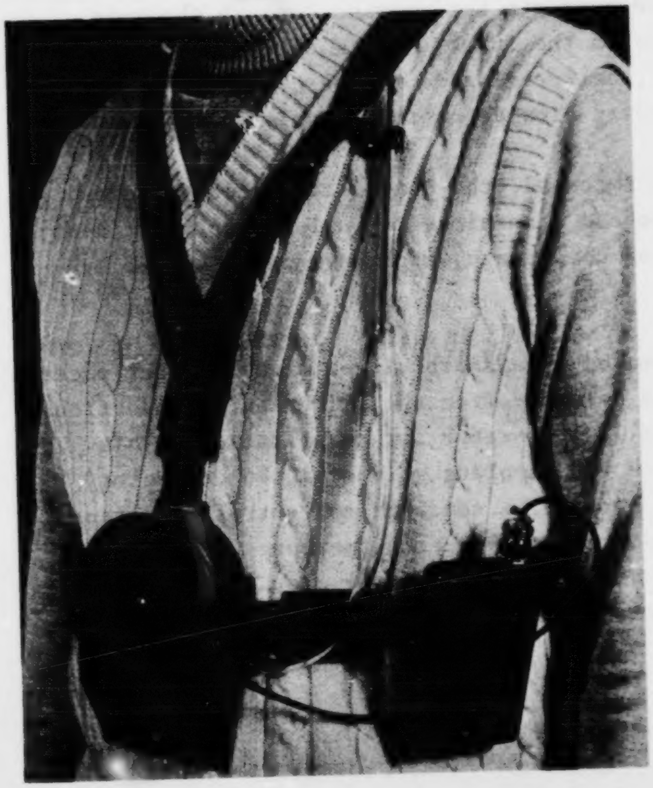

FIGURE 4. Personal monitor in use.

60-Hz source by means of the power line from the back of the case. The five-prong miniature hexagonal connector without the clamp is connected to the matching terminal on the accumulator for use in measuring operations. The readout device can be modified for operation on battery power.

At the start of any sampling operation--after the pump, harness, and accumulator are adjusted on a wearer--the accumulator is connected to the readout unit. With the clear switch in the depressed position and the mode switch elevated, the middle switch is activated. This zeros the accumulator and constitutes the beginning of the sampling interval. The accumulator is then disconnected from the readout. The accumulator commences operating as soon as the zeroing process is completed. However, the clear switch position should be changed immediately to avoid loss of future data when another challenge is made.

The personal sampler assembly may be used for collection of a wide variety of airborne components. Figure 4 shows a typical example of the full assembly set up to collect a gaseous component on a coated tube collector. The collector in this case consists of a 20-cm ceramic tube which is located under the collar clip. It is protected by a tygon sheath. Air drawn from the neighborhood of the wearer's head passes through the tube. The desired pollutant is collected on the inner surface of the tube by an appropriate coating. For example, sulfur dioxide may be collected on a coating of sodium carbonate, and nitrogen dioxide on triethanolamine.

At the end of the collection interval, the coated collector tube is placed in a screw-capped test tube and transmitted to a laboratory for analysis. Table 1 shows a selection of components which have been sampled by the personal monitor technique.

Mercury is quantitatively removed by a short silver wire absorber packed randomly in a 5-cm section. It is desorbed from the silver in an induction furnace and passes directly into a UV photometer for quantitation. This technique is also used to calibrate the sampling volume of the collector/accumulator components. For this purpose, a constant concentration mercury source was set up which gave 5 nanograms-per-liter of mercury vapor. The silver plug collector was used to sample this stream by operation of the personal monitor pump. The accumulator pot was adjusted until the digital readout was 1 ml-per-digit.

TABLE 1

Applications of Personal Monitor

GASEOUS COMPONENT	ABSORBENT	ANALYTICAL METHOD
Mercury	Silver	UV Photometry
Hydrogen Chloride	Sodium Carbonate	Luminol Chemiluminescence (LC)
Nitric Acid	Sodium Chloride	LC
Sulfur Dioxide	Sodium Carbonate	LC or Flame Photometric Detection

The second example utilizes collection of hydrogen chloride on a sodium carbonate coating placed on a small-bore collector tube which is part of the gas inlet line to the pump. The acidic gas diffuses to the wall during passage through the collector and is retained with high efficiency (>95 percent). The collector tubes are returned to the laboratory for analysis. We have utilized a procedure which involves rinsing the carbonate/chloride coating off the tube with a solution of potassium iodate in sulfuric acid. The evolved gas may be quantitated by use of the Geomet luminol chemiluminescence instrument. For hydrogen chloride, collection of about 50 nanograms is required.

Similar techniques are available for the collection and analysis of nitric acid and sulfur dioxide. Nitric acid is collected on a sodium chloride coating. In the laboratory, the analysis uses a sulfuric acid rinse and the luminol chemiluminescence method for quantitation. Sulfur dioxide is collected on sodium carbonate and may be analyzed by a similar luminol chemiluminescence technique or by flame ionization photometry. Nitrogen dioxide may be collected on a triethanolamine coating, diazotized, and read out spectrophotometrically. These methods require collection of 10 to 40 nanograms of the pollutant.

Other applications of the collection technique may involve small columns of absorbent in place of the coated diffusion collector tube. Table 2 shows a number of potential applications. For example, a variety of organic compounds may be collected on styrene-divinylbenzene copolymer spheres such as Chromasorb 102 or Tenax-GC. Thermal desorption into a gas chromatograph or a gas chromatograph/mass spectrometer combination provides analysis.

TABLE 2

Applications of Personal Monitor

GASEOUS COMPONENT	ABSORBENT	ANALYTICAL METHOD
Selected Organic Compounds	Styrene-Divinylbenzene	Gas Chromatography (GC) or GC/Mass Spectrometry (MS)
Vinyl Chloride	Charcoal	GC
Pesticides	Supported Ethylene Glycol Polyurethane Foam	GC/MS
Carbon Dioxide	Hydrazine-Crystal Violet	Spectrophotometry

Likewise, vinyl chloride may be collected on charcoal and desorbed into a gas chromatograph for analysis. Pesticides may be collected on a variety of materials and analyzed similarly. A novel procedure for carbon dioxide utilizes a tube coated with hydrazine-crystal violet followed by a spectophotometric determination of the remaining colored species.

In general, procedures can be devised which are specific and adequately sensitive for most industrial gaseous species. However, care must be exercised to match the sample collector, sample volume, air concentration, and the sensitivity of the analytical laboratory technique.

Although this version of a personal monitor may be used without correlation with the respiration rate of the wearer, a number of applications are of interest in which dosage or exposure data may be obtained.

Table 3 shows a test which compares the volume sampled by the pump with spirometer measurements of the wearer's respiration. In these tests a plastic bag was filled with an air sample and pumped out by the personal monitor pump, which was activated in position on a wearer. The exhaled volume was measured by a simple spirometer. As the data show, in this test about 4.3 percent of the exhaled volume was sampled by the pump.

A second test was run on the same subject after the harness was removed, replaced, and readjusted. Table 4 shows the data from the second test. In this series, about 4.8 percent of the respired volume was sampled.

The difference in the fraction sampled in the two tests was 10.8 percent.

TABLE 3

Respiration Correlation

TEST NO. 1

Sampled Volume (1)	Spirometer Volume (1)		Fraction Sampled
1.590	38.3		0.0415
1.388	30.3		0.0458
1.316	30.1		0.0437
1.601	37.0		0.0433
1.412	34.3		0.0412
		Mean	0.0431
		C.V.	4.3 percent

TABLE 4

Respiration Correlation

TEST NO. 2

Sampled Volume (1)	Spirometer Volume (1)		Fraction Sampled
1.584	31.0		0.0511
1.479	32.1		0.0460
1.362	27.8		0.0490
1.672	33.5		0.0499
1.391	30.7		0.0453
		Mean	0.0483
		C.V.	5.2 percent

This may be considered to be a tentative estimate of the reproducibility of the sampling technique on a single wearer. Obviously, considerably more data is needed on various individuals in a variety of activities before the limits of the correlation are established.

Patent applications on this device are pending.

MAILING ADDRESS OF AUTHORS

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Discussion

PETROVICK: Matt Petrovick, EPA. I had a question regarding your comments on the placement of the device over the abdominal wall. I wonder if you have had a problem in subjects who might be abdominal breathers in one case, and in the other case, thoracic breathers; and how you covered both of those kinds of breathers?

SIBBETT: Actually, our anticipation is that the correlation might be established for each individual. A short calibration with a spirometer or something of that type would be necessary at the beginning in order to have the dosage correlation at the end. In short, I don't know how good a generalized statement is on that point.

STETTER: Joe Stetter, Energetics Sciences. In terms of the way your pump operates, does it pump when the subject is inhaling or exhaling, or at the same time? And if so, would you give us an idea of what the flow rate through the sampling tube would look like as a function over time?

SIBBETT: In general, each stroke is worth about 30 milliliters in each direction if it is a full stroke. In normal respiration--meaning with the subject at rest--about 40 percent of the time is actually involved in movement of the pump.

Roughly 60 percent of the time the pump is inoperative.

BEADLES: Bob Beadles, Research Triangle Institute. You have an interesting portable, self-powered device. Do you have any idea of what the electrical equivalent power might be with it? You can use it in a variety of ways. But in a very simplistic way you can drive a super miniature electrical generator with it. What is the equivalent power?

SIBBETT: I don't know. We have used these accumulator modules with the 9-volt batteries since last September. The 9-volt charge does quite well for the data storage.

MAGE: Dave Mage. Bob, you were asking if there were an electrical conductor moving in a magnetic field could you power your microprocessors?

BEADLES: Absolutely. That is the question.

SIBBETT: Almost anything is possible with microelectronics.

WOEBKENBERG: Mary Lynn Woebkenberg, NIOSH. I was wondering if you had tried the pump with the commercially available sorbent tubes and charcoal tubes?

SIBBETT: If you are talking about the kinds of things that adsorb gases, I did try them. The pressure drop is too great.

WOEBKENBERG: What about the smaller charcoal tubes, where the drop isn't quite as large?

SIBBETT: Actually, in principle, of course, here you would like to limit the pressure drop as much as possible through the adsorbent. We have done a fair amount of work for NASA on dosage measurements in the field. We find that--in regard to dosage measures on chemically coated tubes--that a simple coating, say 5 percent sodium carbonate in the case of an acidic component, lasts almost indefinitely. We have never really faced a case of the concentrations to be collected being high enough to exceed the capacity of the tube.

DOCKERY: Doug Dockery, Harvard. Did you say who is supporting this research and what the purpose of it is?

SIBBETT: Up to this point, nobody has really supported it. The purpose of it is quite clear: to develop a unique individual monitoring or sampling procedure which may be of use in pollution studies of the type that we have talked about earlier today.

The company I work for is involved in a fair amount of computer modeling studies of exposures. This is just sort of a natural attachment to some of the other things that they do.

Personal Monitor Cosmetology: An Aesthetic Approach

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Currently, environmental and human health effects data are collected and evaluated by techniques involving fixed-monitoring stations. The advantages of and requirements for personal monitoring devices are being considered to enhance the current devices to perform the environmental and health effects surveillance function of air quality evaluation programs. An ideal personal monitor system should: 1) record both physiologic and environmental parameters simultaneously; 2) be reasonably priced, personalized, lightweight, portable, and suitable for use by human subjects; and 3) contain a solid state memory with short-term data storage and data transfer capability. Few such functional personal monitors exist in the desired configuration, although the technology for development and fabrication is well known. The role of personal monitors in environmental and health effects research has been reported earlier (1). The purpose of this paper is to 1) place in perspective the physiologic and health consequences of environmental pollution in terms of the pollutant sources, 2) develop guidelines as to how the physiologic monitoring process might take place; and 3) present and display prototypes of "personalized" personal monitors, particularly for the female segment of the population to be studied.

POLLUTANT SOURCES

There are several types of pollutants which have been shown to affect the environment as well as the health of animals and humans. These include atmospheric gases, aerosols, particulate matter, pesticides, toxic substances, odors, noise, and radiation. Gaseous pollutants such as carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), nitric oxide (NO), peroxyacetyl nitrate (PAN), and hydrocarbons (HC) are products of automobile exhausts, power plants, and industrial exhaust gases due to the combustion of fossil fuels such as coal and oil. The pollutant gases are generated as the by-products of combustion and incomplete combustion, such as the generation of SO_2 from oxidation reaction of sulfur in fossil fuels. Complete combustion of the fuels would produce carbon dioxide and water, which are not considered to be pollutants. Carbon monoxide and hydrocarbons are products of incomplete combustion. Nitric oxide is produced when the nitrogen is oxidized by the high temperatures of combustion. The internal combustion engine of the automobile is the principal source of atmospheric NO and NO_2 pollution.

The ultraviolet energy of sunlight induces the oxidation processes to form the photochemical oxidants. The photo-oxidation converts NO into NO_2, O_2 into O_3, sulfur dioxide (SO_2) into sulfur trioxide (SO_3), and generates the unstable PAN compounds due to the irradiation of nitrites in air or oxygen (2).

The formation of pollutants within the environment is the product of a complex atmospheric chemical process. The atmospheric level of each pollutant is dependent on atmospheric conditions, number and quality of combustion sources, and the surrounding topography. The conversion of photochemical oxidants is directly related to the amount of available sunlight and temperature of the polluted air mass. The available light is not only dependent on cloud cover, but the amount of photochemical aerosols in a given polluted air mass, which are themselves by-products of the interactions of the photochemical oxidants. The dilution of air pollutants is affected by winds, temperature inversions (which prevent pollutant dissipation into the atmosphere), and elevation or air density. Other types of airborne pollutants include aerosol sprays (hair, paint, and agricultural pesticides), industrial solvents, and fine particulate matter (coal dust).

Noise sources have been shown to be harmful above 80 decibels A-weighted sound level (dBA), and those annoying to the major segment of the population are considered by the Environmental Protection Agency as pollution (3). Environmental noises are produced by a wide variety of sources; for example, automobiles, construction equipment, transport trucks, commercial aircraft, and steel mills. Noise sources may be fixed, moving, transient, or temporary, and may range in sound level from an average of below 35 dBA found in the suburban home, to over 110 dBA measured in and around mineral mine operations. Two hundred feet from a jet at takeoff, the sound level is 120 dBA (4,5,6). Many industrial and transportation noises are above the 90 dBA maximum 8-hour

Occupation, Safety, and Health Act (OSHA) exposure level. The reduction of excessive noise levels at the source, and providing adequate hearing protection to the exposed population, is clearly of interest to the health sciences as well as to the regulatory agencies.

Human exposure to electromagnetic radiation is extensive when the exposure from industrial, medical, and scientific devices is combined with the exposure to home equipment, radio, FM, TV stations, military and civilian communications equipment, navigational aids, and radar. The sources that produce ionizing radiation are X-ray and radioisotope equipment, nuclear power plants, atomic blasts and weapons testing, and solar radiation. Although the physical characteristics of electromagnetic and ionizing radiation are well understood, their impact as environmental pollutants is less clear.

HUMAN HEALTH EFFECTS OF ENVIRONMENTAL POLLUTANTS

Environmental pollutants can affect the health of individuals in a variety of ways, ranging in severity from physiologic changes of uncertain consequence to pathologic changes leading to disability and, sometimes, death. The more severe effects, such as chronic long-term illness and death, are manifest in a relatively small portion of the population over a long period of time, and they are difficult to quantify because other complex factors difficult to quantitate are usually associated with death. At the other end of the spectrum, slight physiologic and pathologic changes may not be detectable with the degree of certainty desired because of the unique ability of the human body to respond to and recover from most types of environmental insults. Adverse health effects may result from short-term or long-term pollutant exposure. Many factors contribute to differences in the distribution of diseases associated with air pollution exposure, such as age, sex, race, occupation, cigarette smoking habits, geographical location, etc. The health effects discussion that follows is based on appropriate statistical adjustments for these factors in assessing their environmental health effect impact.

The vast majority of environmental pollutants are airborne and gain access to the body via the respiratory tract (i.e., the lungs). Depending on the particle size of the pollutant, its chemical composition and activity, the effect of the pollutant may be restricted to the respiratory tract, or it may be absorbed via the blood stream and exert its effect indirectly on another target organ. A few pollutants have a direct effect on body tissue and organs, such as, for example, radiation and environmental contaminants that irritate the external layers of the eyes. Other pollutants appear to affect the brain and central nervous system and to indirectly produce changes in behavior, control, and coordination of human activity. There are a wide variety of human health effect responses that are yet to be identified, because they have not been examined thoroughly and systematically.

Basically, when foreign matter is introduced into the human airways, the natural respiratory response is to expel it through the action of hairlike cells sweeping the material out, washing the surfaces with mucus which is constantly being secreted, or by coughing the material into the mouth for expulsion or elimination. Environmental pollutants act to increase the secretory activity of the mucous cells (or inflame them), and inhibit the action of the special hairlike "scrubbing" cells, thus producing an increase in frequency, duration, and intensity of the compensatory cough mechanism. Irritation of the mucous cells causes them to swell and partially occlude the airway, making breathing more difficult (i.e., increasing airway resistance). Decreasing the activity of the "scrubber" cells produces a stasis of mucus material which constitutes an excellent culture medium for the growth of bacteria and infectious agents within the lungs and airways.

The site of irritation may be in the upper airways, small (lower) airways, or within the lung tissue itself. If the inflammation reaches the gas exchange tissue (alveoli), normal exchange of needed O_2 and unloading of CO_2 is impaired. The greater the area of inflammation, the greater will be the resulting decrease in lung function, or impairment of gas exchange. Chronic inflammation increases tissue susceptibility to infection with pathogens. NO_2, for example, has been shown to be related to an increase in incidence of respiratory infection in humans (6).

Basically, any irritation which produces an enlargement and inflammation of mucous cells within the airways and increases secretions will decrease the potential air volume which can be taken in and expelled and will affect normal respiratory function. Focal irritation of large airway channels may produce a substantial reduction in the lumen at that point. Air moving through this constricted area can produce turbulence which in turn can be heard through the chest wall as "wheezes" and "rhonchi." The greater the luminal constriction, the more intense the turbulence and subsequent sound produced for a given respiratory effort.

Environmental pollutants like NO_2, O_3, and SO_2, produce changes in respiratory airway membranes which in turn alter pulmonary function (6,7). SO_2, for example, is highly soluble in water (forming H_2SO_3 mist) and is usually absorbed quickly in the proximal parts of the respiratory systems; hence, principal effects are seen in the upper respiratory tract. NO_2 and O_3, on the other hand, are not as soluble in water and in the upper respiratory tract. Their effect is seen in the smaller airways and in the lung tissue itself. Epidemiologic studies have shown a greater incidence of respiratory infections and a decrease in pulmonary function in people living in an environment high in NO_2, O_3, and SO_2, compared with those living in a relatively pollutant-free environment (6). O_3 is also a powerful chemical oxidant and recently has been shown to produce a radiomimetic (radiation-like) effect on peripheral blood cells. Ozone has been shown to produce an increase in chromosomal breakage of peripheral leucocytes--about 10 times that of nonexposed subjects.

Carbon monoxide traverses the alveolar membrane and combines with the hemoglobin in the blood to form carboxyhemoglobin. As a consequence, hemoglobin--the iron component of blood, normally used to carry oxygen to the tissues--is rendered less effective. The net result is that the end organ or tissue, dependent on the oxygen carried by the hemoglobin, is less efficient at performing its principal function. Recent studies have shown that the heart must work harder in order to do the same amount of work following exposure to carbon monoxide than before carbon monoxide exposure. In healthy young people, these changes go almost undetected, due to the intrinsic ability of the heart to compensate for the slight compromise in oxygen-carrying capacity. In subjects with pre-existing coronary vascular disease, the changes produced in cardiac function are more obvious and detrimental to the individual's health (8,9).

Radiation has been shown to produce a direct effect on cellular function because of its ability to penetrate surface and deep structures. Excessive ambient noise levels have been shown to produce an effect on human performance, presumably due to interference in the reception sensory nervous signals by the brain from multiple pathways (i.e., auditory, optic, tactile, etc.) during the performance period.

The major adverse health effects observed thus far have been associated with the respiratory system, mainly because of the respirable nature of airborne environmental contaminants and, to a limited extent, because of the cardiovascular system and central nervous system. It is unclear (and indeed unknown) to what extent and in what manner environmental contaminants affect other organ systems, such as the kidney, the reproductive system, and skeletal muscles. Eventually, each possible health effect should be explored in a short-term and long-term exposure schedule in order to obtain the most complete information regarding the relationship between environmental pollutants and adverse human health effects.

PERSONAL MONITORS

Currently, environmental and health effects data are collected and evaluated through a combination of techniques, including data from fixed environmental monitoring stations. Increasing public concern and national priorities have dictated the need to expand the current data collection base to include more detailed surveillance of a wider range of pollutants and a more comprehensive evaluation of individualized health effects. In this context, the development of personal monitors which measure physiologic and pollutant events simultaneously are being proposed. Comprehensive personal monitor capability will permit accurate monitoring of pollutant data and the concomitant physiological response within the immediate vicinity and physical location of the subject at all times.

Personal monitors are envisioned to serve as a means of providing a more meaningful scientific relationship between the physiologic and environmental pollutant exposure in human subjects. More specifically, a need appears to exist for an individualized "early warning health effects surveillance system" designed to sense and process physiologic responses and environmental pollutant data simultaneously. Ideally, a complete physiologic monitor system would include invasive and noninvasive clinical evaluation techniques. Practically, however, only noninvasive techniques are being considered.

An ideal personal monitor should be able to process and correlate simultaneous physiologic and environmental pollutant measurements at a scientific laboratory level of accuracy coupled with short voice comments from the subject. It is imperative that multilevel feedback capability be available to document the subject's assessment of discomfort relative to environmental conditions, such as symptom reports, location, and general environmental conditions. Such feedback capability has been shown to be invaluable in the assessment of data collection and analysis programs in the past.

Physiologic Monitoring

With the many physiologic variables to monitor, it is unreasonable to consider burdening the subject with an excessive number of transducers and associated equipment which may be cumbersome and physically unattractive. The transducer-to-anatomy interface and the transducer-to-pollutant interface must be considered in any final personal monitor design. Ideally, transducers could be optimally placed on male and female subjects to provide for the measurement of multiple physiologic parameters. For instance, a piezoelectric transducer designed to respond to acoustical energy might also measure simultaneously pressure transients, voice, ambient noise, heart sounds, heart rate, and cough. The incorporation of appropriate electrodes within the piezoelectric transducer housing can provide the measurement of the electrophysiologic activity of the heart (electrocardiogram). From specific signal conditioning and filtering techniques of the complex acoustic (pressure) and electrophysiologic signals, a variety of additional relationships may be derived which are not otherwise available from a single transducer. This design provides the basis of an "integrated transducer" which would have the capability of recording more than one phenomenon from a single transducer at a single anatomic site.

1) Respiration-Pulmonary. Pollutants may cause irritation of the mucous cells which line the respiratory tract, resulting in the reflex production of a cough. Increased mucosal irritation, in turn, may cause narrowing of airways, resulting in respiratory wheezing produced from airway turbulence. Cough events may be detected and quantitated from the placement of a piezoelectric transducer over the lower abdominal wall to register cough diaphragmatic pressure. Additional respiratory parameters, such as the ventilation rate (breaths per minute) and indirect respiratory volume, may be detected by changes in thoracic geometry by electrical impedance or pneumographic techniques.

Transducer-to-anatomy interface differences that exist in males and females may be circumvented by installing the appropriate transducer within the structure of conventional garment wear. For example, in female subjects, the transducer for heart sounds may be placed in the base elastic strap of the bra over the anatomic apex of the heart; for wheeze registration, the transducer may be placed within the rear bra strap area of the shoulder blades; coughs may be recorded from a transducer placed within the abdominal wall panel of panty hose.

It is well known that some people are "chest breathers," while others are "abdominal breathers." In either case, the respiration rate transducer might be a small pneumatic tube connected to a semiconductor transducer. For "chest breathers," the transducer might be incorporated in the base elastic strap of the bra (for female subjects); for "abdominal breathers," the transducer might be incorporated in the abdominal panel of panty hose.

2) Cardiovascular-Heart. The personal monitor system should provide the capability for sensing and characterizing the electrophysiologic and hemodynamic events of the vascular system and heart. Typically, electrophysiologic information is obtained through the electrocardiogram (ECG), and hemodynamic information is usually obtained from the arterial blood pressure (BP).

The ECG measurements may be made with as few as a single pair of bipolar surface electrodes, or with as many as 12 electrode combinations, depending on the thoroughness of the electrocardiographic examination. The ECG waveform is characterized by the P-QRS and T features which correspond to specific electrophysiological events throughout the cardiac cycle. From this electrical information, basic heart rhythm (heart rate), and the position of the S-T segment of the waveform with respect to the isoelectric baseline, are important determinants. Often, abnormal rhythms (arrhythmias) and shifts in the S-T segment of the waveform occur under a variety of conditions, particularly when oxygen (carried by the blood) is unavailable to the contracting heart. Recent studies (8,9) have shown that exposure of subjects to 100 ppm (parts-per-million) carbon monoxide (which decreases effective oxygen delivery to heart tissue) produces a detectable shift in the S-T segment of the ECG during exercise in normal healthy subjects.

Quantitation of the cardiac rhythm and the degree of S-T segment deviation from the baseline may be accomplished with a special-purpose S-T segment microprocessor integrated within the personal monitor system. Specific features such as S-T segment duration, S-T segment amplitude (positive and negative), and rate of change (first derivative) of the S-T segment are most important and significant in assessing specific adverse cardiac health effects in response to pollutant exposure.

The measurement of blood pressure may be accomplished by affixing a piezoelectric transducer to the radial artery of the arm in such a way as to detect maximum (systolic)/minimum (diastolic) arterial pressures, pulse pressure (systolic minus diastolic), and heart rate.

Valuable cardiac performance information may be derived from the directly measured cardiovascular parameters. For example, heart rate from the ECG through a conventional cardiotachometer, and systolic time intervals (STI) from the combination of the phonocardiogram, the electrocardiogram, and blood pressure. STI's provide information relative to the rate and duration at which the heart is contracting and relaxing. The triple product combination (heart rate, mean blood pressure, and ejection time of the heart) serves as an index of the amount of oxygen the heart is consuming during the process of contraction.

3) Central Nervous System. The central nervous system activity (electroencephalogram, EEG) is one of the most difficult signals to interpret in that responses are often subtle and difficult to quantitate. Detection of behavioral

patterns associated with changes in the EEG or the electro-oculographic potentials (EOG) may be accomplished, but not without carefully planned and executed experimental programs.

Central auditory responses are related to the temporal lobe of the brain; recording of the EEG over the temporal area of the skull may provide an index of auditory time discrimination judgments by a given subject. Recent studies suggest that auditory time discrimination shows a decrement after exposure to 100 ppm of carbon monoxide for 4 hours.

The human eye is (as is the lung) directly exposed to environmental contaminants. Eye irritation can produce increased frequency of eye blinking, fatigue of ocular musculature, and pain sensation. Eye blinking activity may be monitored with silver chloride electrodes placed laterally and slightly posteriorly to the eyes. Appropriate signal conditioning of the EOG signal could provide a reliable electrical representation of an eye blink, blink rate, and duration. Additional conditioning of this electric signal (such as the first derivative) may provide information of ocular fatigue relative to normal and abnormal environmental pollutant exposures.

4) Other. Tracking the location of the subject with a personal monitor within a given geographic area will provide an additional means of referencing and characterizing pollutants in a given area at any time of day, in contrast to a fixed-station operation. Tracking may be accomplished as a function of verbal or coded location reports into the system memory from the subject. The monitoring of radiation, for example, might be coupled with location and radiation film badge exposure levels through a similar process.

Data Acquisition System

The data acquisition system (DAS) design for personal monitors may be implemented in a variety of ways, any one of which appears to require state-of-the-art techniques. Physiologic transducers and air pollutant transducer signals are different in nature; hence, a properly designed DAS must take these differences into consideration. Most physiologic responses are dynamic, rapidly changing, and almost periodic functions of time. Air pollutant levels are usually static or change slowly in time. Therefore, the dynamic frequency response of each transducer is an important consideration.

All transducers are subject to various forms of artifact (physiologic, 60 Hertz, movement artifacts, pollutants, interference from other contaminants, etc.). The judicious rejection of these artifacts is an important factor for reliable DAS design. To ensure maximum DAS stability and reliability, it is important to select a physiologic event as a time reference with which to sense and reject any artifact from the system signals. For example, in detecting a cough, a microphone or another appropriate acoustic transducer may be employed. Coughing is an acoustical signal produced during the expiratory phase of the respiratory cycle. Any acoustical signal sensed by the cough transducer during inspiration (such as talking, ambient noise, etc.) must be rejected. However, during expiration, the expiratory gate would open for any possible cough data that might occur.

All data collected on board the personal monitor might be stored in digital form in solid state memories for subsequent playback, processing, and display. The system should have the capability of recording data for 24-hour periods, after which the data could be read out into a long-term storage device for inspection and analysis. The solid state memory readout could be accomplished by a variety of ways; i.e., dataphone interface to local or regional fixed stations.

A complete system design must consider playback, display, and processing functions, which in turn are determined by the nature in which the data are recorded. The system design should consider options to perform a wide variety of information processing procedures, such as signal averaging, digital filtering, tread analysis, and interactive graphics. Ideally, provisions to process the personal monitor information should include on-line and off-line capabilities. This capability is currently available with low-cost, high-efficiency microprocessors.

PERSONALIZED PERSONAL MONITORS

Personal monitors are envisioned to provide more reliable physiologic and environmental information on human pollutant exposures beyond the range and capability of community health surveillance stations. Specifically, a need appears to exist for individualized surveillance systems to sense and process physiologic and environmental pollutant data simultaneously. Devices have been developed to satisfactorily detect environmental contaminants and their physiologic consequences. Fabricating these detection devices to ensure user cooperation has not been a simple task. Compliance and user resistance problems are particularly sensitive when dealing with the female segment of the population to be studied.

An attempt was made approximately 9 years ago to incorporate the (then) state-of-the-art technology related to turning simple physiological and environmental monitors into devices that were portable, lightweight, and reasonably priced. Pilot feasibility studies were conducted to evaluate the effectiveness and practicality of personalized personal monitors, particularly those which female subjects would be required to carry or wear. The remainder of this presentation will deal with the results of the feasibility studies, in which specific pollutant and physiologic monitoring devices were incorporated with specific pieces of jewelry which are not only scientifically functional, but also attractive.

1) Oxygen Pendant (Figures 1 and 2). A photo cell mounted in the pendant senses the continuous samples of ambient air. When the level of environmental contamination exceeds a preset threshold, an audio device is triggered electronically which alerts the subject to the presence of pollution. The pendant also contains a mask and a 10-minute supply of oxygen. This device may be especially useful to subjects with a pre-existing respiratory disability such as asthma. In these cases, the oxygen canister might also contain a bronchodilator to relieve the distress and discomfort associated with an asthma attack.

2) Heart/Pulse Sensor Bracelet (Figures 3 and 4). A piezoelectric transducer relays the peripheral arterial (radial) pulse to circuitry which activates a light emitting diode display device. Heart rates above the preset threshold for an individual enables an oscillator to emit an audible frequency, the output of which is connected to an earphone speaker to produce a warning sound which alerts the subject to check his/her activity level, take appropriate medication, or seek professional assistance.

3) Body/Air Sensor Belt (Figures 5 and 6). This belt is made of stainless steel and liquid crystals designed to monitor toxic gases, ultraviolet radiation, and air and body temperature. Increasing doses of X-ray radiation progressively lower the color play range of cholesteric-phase liquid crystal materials. The effect is enhanced when an effective amount of an iodine-containing compound is used in the liquid crystal material. Novel iodine-containing compounds in the appropriate proportions give direct indications of the dose of X-ray radiation that has been received.

A layer of water-soluble plastic material is first deposited on a limb or torso to serve as a barrier layer. A cholesteric layer is placed over the barrier layer. A chromatic display of temperature of the limb or torso will

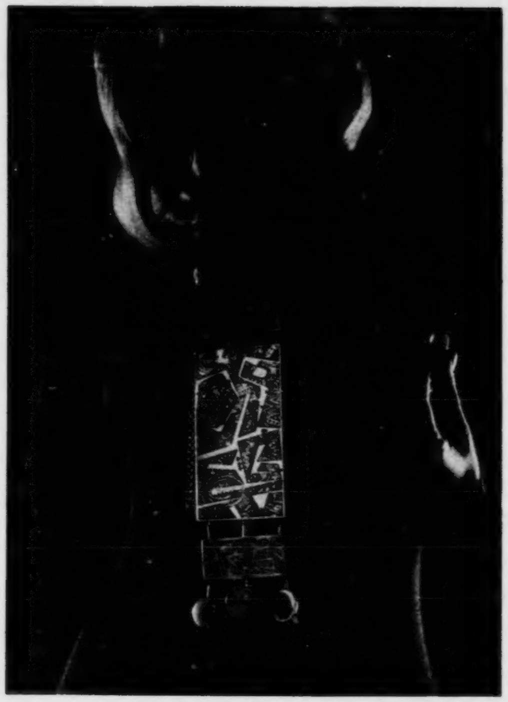

FIGURE 1. Oxygen pendant (normal closed position).

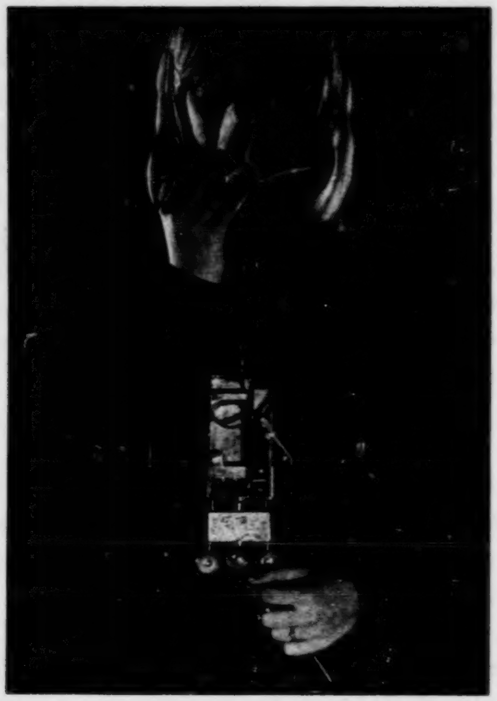

FIGURE 2. Oxygen pendant (open position with mask and canister exposed.

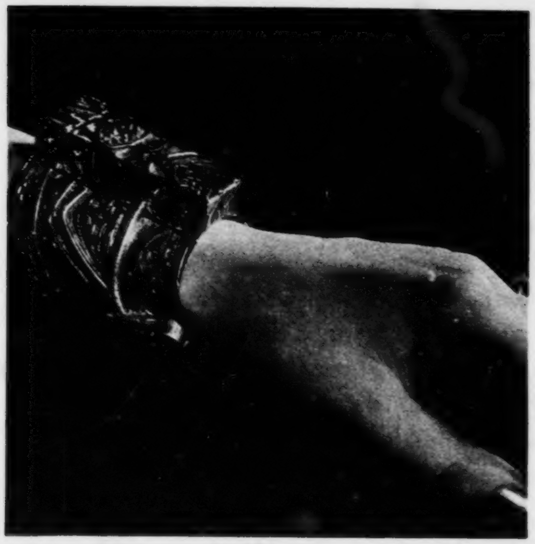

FIGURE 3. Heart/pulse bracelet in place on hand.

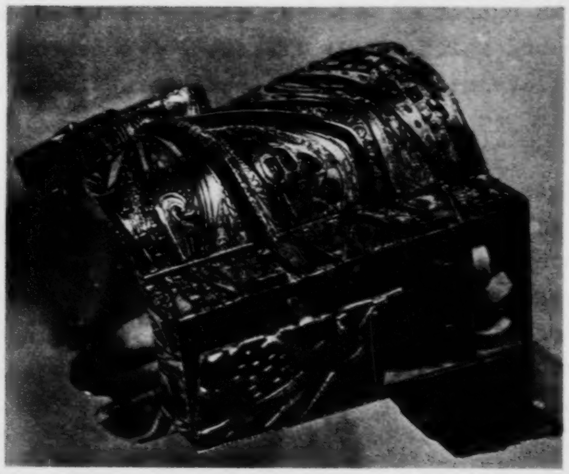

FIGURE 4. Heart/pulse bracelet with electronics and compartments exposed.

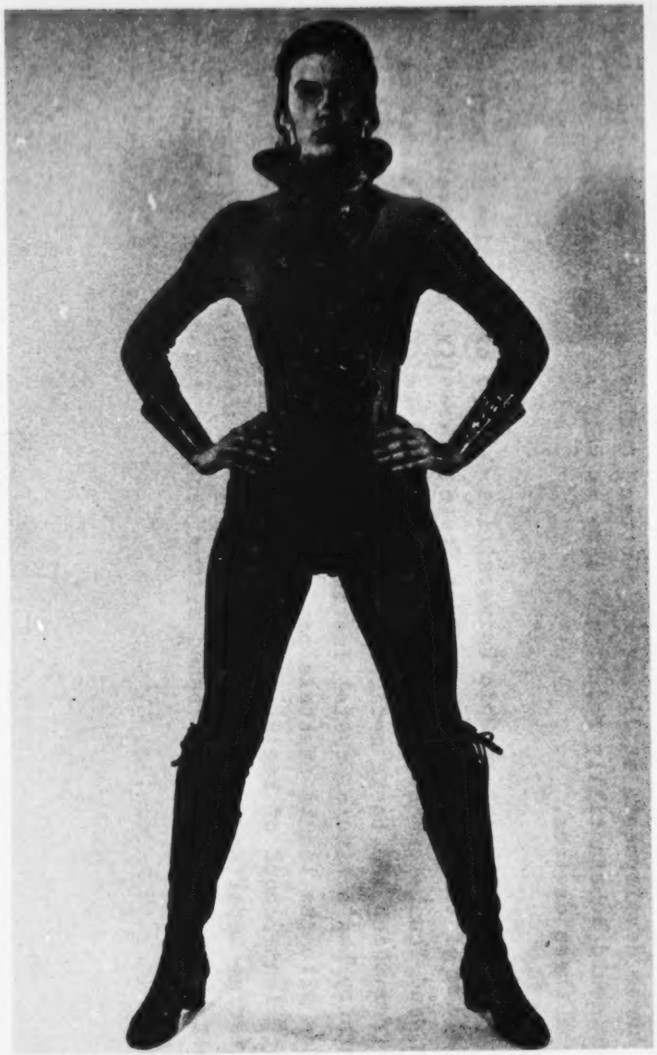

FIGURE 5. Body/air sensor belt.

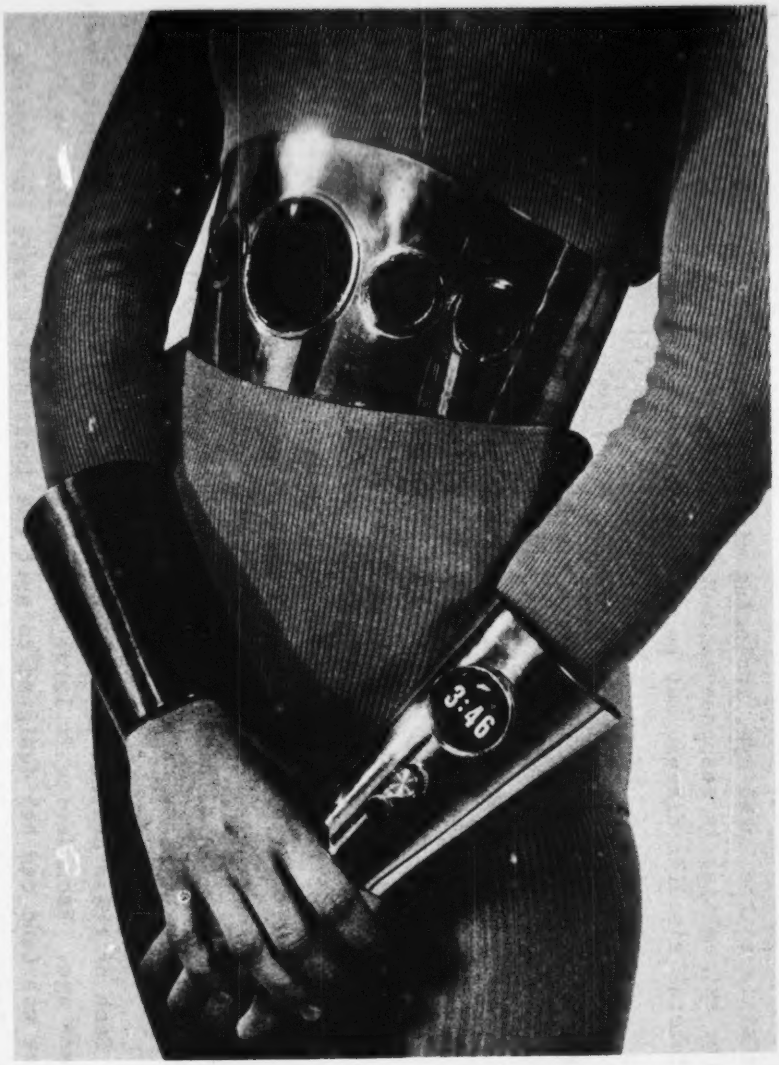

FIGURE 6. Body/air sensor belt and arm bracelet.

be visible to the naked eye, including minute variations. Vasoconstriction in the extremities in response to smoking and the vasospastic effects of peripheral vascular disease may be clearly observed.

4) Liquid Crystal Heart Beat Display (ECG) (Figures 7, 8, and 9). A monitoring electrode is attached to the body to transmit the ECG through electronic circuitry to activate a liquid crystal display of the subject's electrophysiologic heart pattern. Abnormalities in either the rhythm (or rate) or the waveform will be manifest in an aberrant chromatic pattern.

5) Tracheotomy Necklace (Figure 10). An adorned standard medical device fits into an opening, which is surgically performed on the trachea, to permit ventilation. The tracheotomy device is available in sterling silver and silicone plastic through conventional medical supply sources. The tracheotomy necklace is constructed of gold, silver, gemstones, chain, and other materials which may change the clinical appearance of the equipment, permitting it to be viewed as a necklace rather than as a prosthetic device.

Each of these devices was designed utilizing the technology of approximately 5 years ago. Each device is large and obvious to attract attention. Each device was (and can be) designed to suit the individual's taste and physiognomy. Since the time of the original design and feasibility studies, further developments in this area have nearly ceased due to the lack of appropriate interest and support. However, the needed facilities and interest to continue with these developments still exist. Current technology and fabrication techniques could substantially reduce the size as well as the weight and cost of each of these devices.

The Northeastern Ohio Universities College of Medicine is part of a consortium of three universities--Kent State University, the University of Akron, and Youngstown State University. The College of Medicine serves as the base from which the basic medical science studies are conducted. Kent State University has a Liquid Crystal Institute at which further and continued studies with the liquid crystals may continue. The University of Akron has an excellent School of Engineering, within which exists a competent Electrical Engineering Department capable of developing and implementing any microcircuitry and microprocessor-based system required for further development in this area.

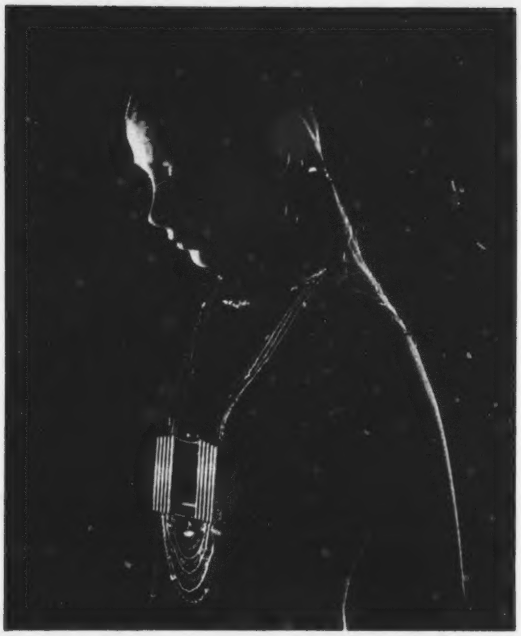

FIGURE 7. Liquid crystal heart beat display necklace.

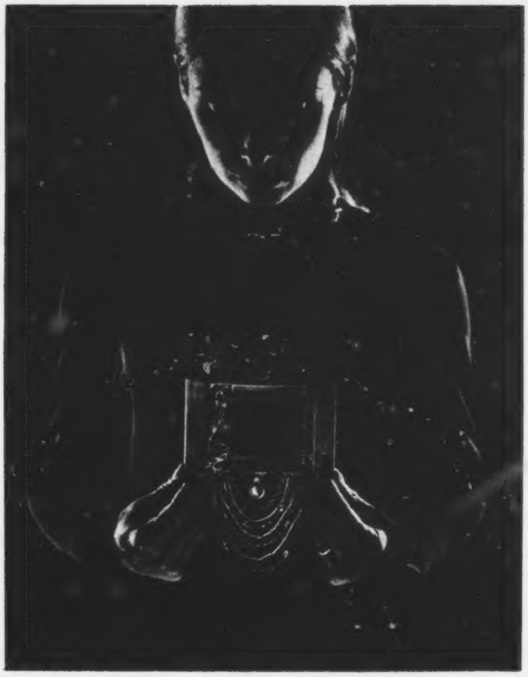

FIGURE 8. Liquid crystal heart beat display necklace (electronics open and exposed).

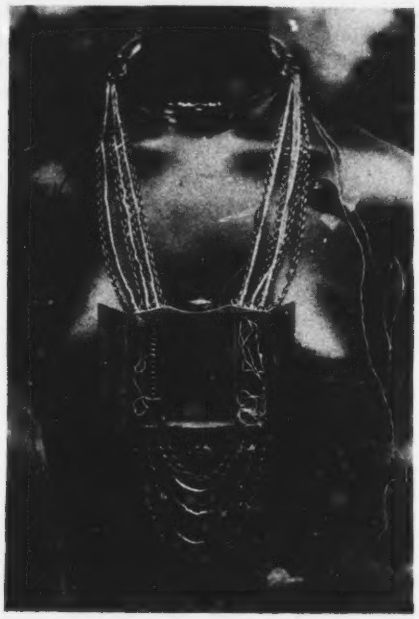

FIGURE 9. Liquid crystal heart beat display necklace (electrode placement and electronics exposed).

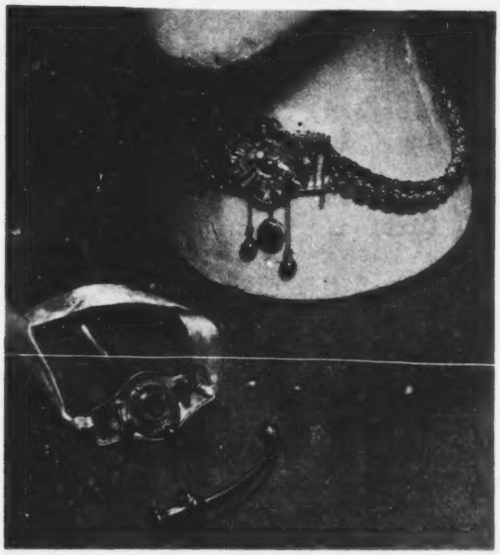

FIGURE 10. Tracheotomy necklace.

ACKNOWLEDGEMENTS

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MAILING ADDRESSES OF AUTHORS

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Discussion

PETROVICK: Matt Petrovick, EPA. Dr. Malindzak and Ms. Scherr, I would really like to commend you for a very unusual and very well designed approach to looking at physiologic measurements in the female. The female happens to be one of the most ignored subjects in terms of science and in terms of data acquisition.

I believe your design approach is going to have a significant impact in placing our health effects data base into balance, which presently I don't think it is.

WALLACE: Who supported this development?

SCHERR: This work? I do.

MALINDZAK: Totally and completely.

SCHERR: I am an Associate Professor of Art at Kent State University. My interest in this subject started with seeing a woman who was very disturbed--cosmetically disturbed--with the hole in her throat, and who wore many scarves to mask herself. And I managed to see in my mind in one brief moment this piece of equipment, and I asked her if she would like me to design something that would be a little bit more interesting. And I did. And that set the stage for another whole wave of research.

I think that maybe I am more or less a scientist, although I could never compete in this area. I am a reactor. And in reacting to this lady, along with the television programs of space technology and watching the space program, I decided at this time to get involved in programs where maybe we could monitor ourselves. And that was my own reaction to it.

I started then in all of these areas, trying to find devices that would monitor anything. So, this is why is all started.

"Shirtsleeve Workshop"

An informal session designed to arrive at a consensus on present abilities of commercially available instrumentation and promising avenues for future research

DR. DAVID MAGE: This evening we would like to discuss informally some of the aspects of personal monitoring that we have gone over more formally during the meeting.

We have heard several papers about personal monitors for exposure and for physiological variables. Some of us have been trying to act as a kind of marriage broker to see if we could merge the two to fit into the same package--we really see that as a necessity. We would like to have some discussion as to the needs that the different Government agencies have in this area. We will have people from NIOSH, EPA, and other agencies speak on what they perceive as being the needs for their agencies.

We would like to make it apparent to the people in industry as to where their markets might be, and we want to stimulate competition to produce the devices that we need to do our job.

The bottom line, I guess, is that, as Congressman George Brown said in his keynote address, we have to show that our approaches to air quality standards are reasonable, let alone correct. In order to do that, we have to be able to demonstrate that people are being exposed and people are having health effects from that exposure. It is one thing to put someone in an environmental chamber and give him 0.4 ppm ozone while walking on a treadmill and then document that he has had some kind of physiological response. But then somebody can ask us, "Well, how many people on treadmills in Los Angeles are breathing 0.4 ppm ozone," and, you know, we can't say 1, 10, 100, or 1,000.

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It becomes very difficult to quantify. As soon as it becomes difficult to quantify, then it can also become very difficult to establish that we are being reasonable. Can we state beyond the shadow of a doubt that there are 100, or 1,000, or 10,000 people who are having health effects?

If industries talk about their cost of pollution control, they talk in units of billions of dollars. Can we justify this cost on the grounds that there is a benefit to the public in terms of billions of dollars?

What I would like to do now is turn this portion of the meeting over to Dr. Lance Wallace for some informal remarks. Some of the things we would like to do is discuss with you some of the needs that we perceive for developments of personal monitors. We would like people to let us know some of the problems that they perceive; for example, that perhaps we haven't been funding you when you have been submitting proposals to develop those monitors that we would like to have.

I would like to get the discussion out informally so that we can have some good interchanges among us.

DR. LANCE WALLACE: I feel that my horizons have been opened up quite a bit by this meeting. I came here thinking of personal monitors basically as being chemical and physical sensors, and by the end of 2 days, I have realized that there are physiological measurements that can be made. There are the cosmetological aspects. There are the microcomputer aspects. It appears that we are on the verge of something considerably larger than I had envisioned.

So, with that as a bit of an apologia, I will mention that what I have done for the past 2 weeks before coming here was to ask the different offices within EPA what chemical and physical measurement devices they felt were necessary and what pollutants they felt were important to develop personal air quality monitors for. As I mentioned in my talk, the Office of Research and Development acts as a service organization to some of the other program offices within EPA. They express their needs for research, and we try to accommodate them.

I spoke to several of the offices that are the most involved with this topic, including the Office of Air, Noise, and Radiation, which includes the Office of Air Quality Planning and Standards and the Office of Mobile Sources. These offices have somewhat different areas of responsibility, and different needs for personal monitors. I have obtained from the people in those offices lists of the pollutants for which they see a high priority for developing personal monitors.

I have also spoken to the Office of Toxic Substances and received the same sort of list from them, and to the other offices within the Office of Research and Development and have received their nominations for high priority pollutants.

But as a sort of straw man, it might be desirable for us to look at the lists that we have come up with and using those lists to investigate the possibilities for using monitors that are already available, that are already out there and can do ambient level measurements, to determine areas in which further research is needed.

I would like to pass out these lists, and I will read them over with you.

Within the Air Office, the Office of Air Quality Planning and Standards' staff members were mostly concerned with the criteria pollutants. The pollutants that they found to be most important were carbon monoxide and nitrogen dioxide. They desired that field studies be done as soon as possible for these two pollutants if there were any personal monitors available that were capable of making ambient level measurements.

From what I have heard in the past 2 days, it seems very possible that we do have personal monitors that are capable of being used in field studies--the ESI monitor and the GE monitor, both for CO. Dr. Palmes' NO_2 device also seems possible.

Perhaps before I go any further, I could ask if there are comments about just these two pollutants as to other devices that appear as possibilities for immediate use in field studies? Are there any comments on the Energetics Science's Ecolyzer 9000 series and the GE device that we have?

DR. MANNY SHAW: I am Manny Shaw of Interscan. We aren't ready right now to give you a dosimeter. We are tooling up on a different type of dosimeter that will be of interest. And when I say different "type," I don't mean necessarily a ppm-hour dosimeter. I mean a dosimeter which will alarm at the TLV. I would say that within 6 months to a year we will be able to field test the Interscan TLV alarm dosimeter.

DR. DONALD SIBBETT: Donald Sibbett, Geomet. I feel that with a short validation program, our personal monitor could be used with NO_2. It is a respirable pump driven by the abdomen. It can be used, I think, rather readily with NO_2.

DR. JOHN BACHMAN: One thing that would be of use as far as we are concerned is if some studies could be done on these two pollutants--CO and NO_2--at the same time. We want these data for two reasons: one is to help us set better air quality standards for these pollutants, and the second is to do a better job of assessing total exposure.

One of the reasons those two pollutants had high priority among the people in our office was that the concentrations of these pollutants tend to vary greatly over an urban area relative to certain other pollutants because of the nature of the emissions and the formation.

NO_2 happens to be a secondary pollutant, as everyone knows. CO is a primary pollutant. But they vary with the automobile. It would be of interest to us to do both of these studies at the same time.

DR. FRANCIS BERLANDI: Francis Berlandi from ESA. Looking at the philosophy of the development of the pollutants of interest, I notice that all the pollutants are associated with air quality standards. And noticeably, there is one pollutant here for which there is an air quality standard, and yet there is no interest in seeing that a personnel monitor is available for it.

In particular, I mean lead. In the future we are talking about arsenic and cadmium. I was curious as to whether people didn't feel that there was a monitor capable of making these measurements and that is why it is omitted, or if nobody is really interested in the variety of sources that are available to the person in his or her daily environment where he can actually uptake lead?

BACHMAN: I think we feel that saying fine particulates is our shorthand for saying anything you can measure on fine particulate filters. But in the specific case of lead, right now we feel that the best personal monitor is blood lead. There are other indicators. Because of the total body burden, we have to measure the various pathways.

We felt first of all that a system that was capable of measuring for fine particulates ought to be able to do lead. Second, right now we have some fair indication of total body burden from the human body.

Concerning the other pollutants, by the way, as Lance will go on to talk about, vapor phase organics and some of the fine particulates cover a whole host of things which are not related to air quality standards, but are related to possible hazardous air pollutant standards.

BERLANDI: The reason I bring up the point about lead is that yes, I understand that the body burden is a good indicator of lead exposure. But it hardly provides sufficient data for the state to implement plans to control the lead. We really don't know where individuals are picking it up in their daily lives, whether it be in the home, whether the kids are getting it on the streets or empty lots, or whether they are breathing it in, as opposed to secondary entrained dust.

There could be some very costly strategies implemented which could backfire in the long run. This is why I mentioned the fact that I think the technology is available, and maybe that formally it should be put down here.

BACHMAN: Again, from the program office point of view, talking to the people who set the lead air quality standard, they didn't feel it would be particularly useful in that application at this point.

DR. EUGENE MEIER: Gene Meier, EPA, Las Vegas. Another point is that when our request went out, we were referring to immediate programs. "If we had a monitor available, which one would you want to use now?" And some priority had to come back. These are the first-thought priorities. These are where we actually have programs now and where we feel we need monitors.

Your point is well taken. If we had the programs going on or the people available, we would probably be working in those areas. But right now, the other compounds listed are those which have first priority.

MR. PAUL KIZAKEVICH: Paul Kizakevich from Research Triangle Institute. Admittedly I don't have much of a background regarding the physical monitoring parameters and how they are measured. But in the sense of the physiological measurements that we have talked about, it is expected that the changes we would like to look at would either be transitory or perhaps accumulated over, say, an 8-hour period, over a workday.

My question is: Are there any physical parameters that can be projected to be measured and assessed so they can be compared to such dynamic studies as a physiological response? The accumulation of 24 hours of the pollutant is not going to give very much information in relation to a person's change in respiration rate or something else during his time at work.

WALLACE: At least for the CO, it did not depend on a 24-hour average--we had a continuous readout. The NO_2 is another matter.

KIZAKEVICH: Is that the only parameter that can currently be measured in that sense?

WALLACE: In a continuous way?

KIZAKEVICH: In a relatively continuous or dynamic fashion.

MAGE: Well, I think that of all of the criteria pollutants, ozone needs to be monitored continuously. Our air quality standard may be changed in the future to another averaging time, but it would still have to be monitored continuously.

KIZAKEVICH: You are not talking about the same thing, now. If you put a monitor on an individual over an 8-hour workday and you expect to indicate a health effect perhaps by the severe pollutants in the working environment, are there any physical measurements to compare the physiological measurements with at all, other than to say that the guy went to work for 8 hours, and as a result during that work of 8 hours he just changes his physiology?

WALLACE: You mean rather than CO?

KIZAKEVICH: Anything. I don't care what it is.

DR. EUGENE SCHEIDE: Gene Scheide, Environmetics. Can you include physiological measurements with pollutant measurements on the same scheme? Or are you comparing apples and oranges? But is he saying should we also be monitoring other physiological responses as well as physical parameters--is that correct?

KIZAKEVICH: Well, gathering pollutants over a 24-hour period is certainly not the same as measuring the distribution across the population, because it depends on whether the person moves. I am interested in knowing which parameters can be measured without resorting to gas samples over a 24-hour period. That would provide no information on health effects whatsoever other than ambient levels.

MEIER: It really depends on the objective. In most cases, the objectives are to profile the pollutant of interest, because we already have established that there is a health effect. Now we are trying to find out what its concentration is in various locations in the environment so that we can determine whether our standards are proper and our stations are located in the proper locations.

In addition to that, information provided by personal monitors can give us a better idea of where to locate a limited number of stations in our sampling network. If management comes in and says, "You want 10 stations. We are only going to give you 2," where do we best put those 2 monitors that we have to get the most effective data to rate the health effects?

MR. MATHEW PETROVICK: Matt Petrovick, EPA. That is a rather interesting comment you made. I wonder if you might enlighten me on which specific known health effects you are alluding to?

MEIER: In terms of what? The standards?

PETROVICK: In terms of the standards and/or any pollutant?

WALLACE: Well, we have six or seven criteria pollutants now. The criteria documents point out the levels at which health effects have been noted for those pollutants.

PETROVICK: That is my question. Which health effects and which associated pollutants?

WALLACE: One for each of these six--the six criteria pollutants. It is a different health effect in each case.

PETROVICK: Is it a lung function effect, or what?

BACHMAN: It runs from asthmatic attack, bronchitis, general heart and lung disease, excess mortality, eye irritations. There are all sorts of effects listed, and each pollutant has its own--CO has its own special effects. Each one has a number of effects, and these are documented. This is probably not the proper place to go into documentation of any specific health effects for each of the pollutants.

But I think that the statement made about our personal monitor needs was put well, at least for CO and NO_2. What we were asking was, having established standards already, an initial reason to do this monitoring is to do a better job of assessing the exposure. And that will affect in turn the standards that are processed.

Meanwhile, a second reason is to use these things later in health effect studies. And therefore, you might want to measure the physiological parameters. But when we were asked what we wanted right away, we didn't speak to that issue.

WALLACE: That is not to say that the other effects are known at certain standards. We have a standard. We have documents that were written back in 1970. With the knowledge that was current then, there was a standard set.

So, for those six, one can do pure exposure studies and determine the frequency distribution of exposures for a given population and find out what percent are, say, exposed to levels above what those criteria documents found to be important. That is one aspect.

The other aspect is for those pollutants for which you do not have standards. One is obviously not going to be able to stop at pure exposure studies. And then, your question about the concurrent measurement of physiological parameters becomes more important.

PETROVICK: One last comment. I have a very strong feeling that of the effects that have been identified with the associated pollutants, most of those relationships probably have not been measured in a dynamic sense, such as Mr. Kizakevich was alluding to.

The issue is how the effect was determined and relative to what pollutant, and was it a dynamic measurement or was it a static one? I have a strong feeling that the effect is probably defined on the basis of an interview with a group of panelists or subjects or through medical forms, rather than from a dynamic active measurement right off a person in the mobile environmental condition.

MEIER: That is true. But you don't go out and kill someone to find out what the LD 50 is. You go collect the data that you have available and make your best judgment based on those data. Then you go out with your personal monitor to find out if indeed people are being exposed to those concentrations. And if so, then you go back for further studies, as you might want to do in your case, and look at the physiological factors as well as the concentrations. Then once you get a strong correlation, you are justified in using the other type of monitor. But right now, the only physical fact that you know is the concentration level associated with a health effect.

WALLACE: Maybe I could suggest this: we do have a physiological contingent of sorts here. If they could get together and make some specific recommendations as to the pollutants for which physiological measurements would be best suited to be taken concurrently with the measurements of the concentration involved, that that could be an input to our workshop tonight, and could be reported on tomorrow in a panel discussion by the chairman or some representative of the group who has expertise in taking physiological measurements.

Is that a possibility?

BACHMAN: Lance, wouldn't it be more productive rather than saying for which pollutants, to first of all define the purpose of what we are doing? I presume it would be to learn more about health effects, not just to catalog exposure. And that means you are doing an epidemiological study of some sort, unless you are talking about clinical studies, which is another breed of cattle altogether.

In that situation, I think we have some people here who also know what kinds of general, almost nonspecific, kinds of respiratory symptoms and other symptoms people experience from air pollution. Also, let's talk about what kinds of techniques and physiological measurements would be useful on a continuous and on a personal basis in that regard.

In a general sense, we are getting guidance on what is the state-of-the-art in conducting epidemiological studies with respect to physiological measurements on a personal basis; something that is a little more general rather just related to CO or any other single pollutant.

WALLACE: Let me go on to discuss the entire list.

Another section of OAQPS mentioned two noncriteria pollutants as being high priority--vapor phase organics and fine particulates.

But in the case of the fine particulates, the OAQPS added the reservation that this would be important only if the health effects groups felt that concurrent epidemiological studies could be conducted. I did speak to the representatives of the health effects group, and they thought that a personal monitor for fine particulates would be important and useful.

For the fine particulates, as you know, we have had some discussion as to the proper size cutoff for fine particulates. For reasons that I do not fully understand myself, there are cutoffs that have been chosen at 2.5 and 15 microns.

BACHMAN: The reason for that is because we are going to revise all of the air quality standards by 1980, including the particulate standard. And in doing that, all of us knew that we should look at particle size instead of just garbage particles again--perhaps including chemical composition.

In looking at the array of definitions of respirable particles and fine particles, we found so many different definitions that we felt that another hard look at it was in order, and in protecting the public health of even the most sensitive segments of the population--given that that is our mandate--we asked our health effects group to take a look at what really is a respirable particle.

They put together a team, which came back with its findings. For example, if we want to protect even the mouth-breathing asthmatic, we should look at particles less than 15 micrometers.

The 2.5 micron cutoff comes from the apparently natural distribution of particles in the atmosphere, where certain particles that are formed from gases or condensates fall into a range less than 2.5 microns in diameter, but those particles that are kicked off the ground or are mechanically generated are greater than 2.5 micrometers. That is one basis for the 2.5.

A second basis, which is a little more tenuous, is that is seems to be an area where most subjects tested fall into a similar pattern.

This is an important definition as far as we are concerned. EPA is setting up a network of some 300 stationary samplers for inhalable particulates. It is a strong movement on our part toward measuring the impact of respirable particles on ambient air quality.

So, for people who are making these instruments and are interested in future epidemiological studies, we are looking at these numbers.

The second factor is, as I mentioned before, the chemical composition. We feel that it is important in doing these kinds of studies to look at the chemical composition, as well, in terms of epidemiological studies. So, whatever system is chosen should be amenable to some of the kinds of techniques that are becoming routine, such as X-ray fluorescence to do elemental analysis, sulfates, or other important components of pollutants.

WALLACE: It does appear, just on my understanding from the first 2 days of this symposium--and I know we have our organics contingent coming in tomorrow--that in these two cases of the vapor phase organics and the fine particulates, we do not presently have a working personal monitor capable of doing ambient level measurements.

MAGE: What averaging time are you talking about? Twenty-four hours? Daily?

WALLACE: I think I would even be happy with a week averaging time if that were necessary.

BACHMAN: There are two different needs. Doing epidemiological studies, it depends on the nature of the study that you are talking about, a 1-hour averaging time if you are looking for acute effects or a longer term. But with the organics, we are talking in reality about carcinogens right now. That is what we care about, at parts-per-billion and maybe even lower concentrations. We have a list of hot numbers right now which we are looking at.

So, there are some specific compounds that we are interested in in terms of only semiquantitative analysis to start with, long-term kind of exposures and the lifetime exposures. We need to know what is out there in terms of the kinds of compounds.

We would accept something that is sensitive to low concentrations of a number of compounds, 10 or 12 or 20, maybe. It would be useful in just getting the gross idea of exposure.

Now, there are some techniques that are being used now in terms of stationary sites, but the idea of doing it with personal exposure would be something, of course. And later, as we become more sophisticated in what we are doing, we would be more interested in maybe very quantitative or more quantitative methods for specific compounds and specific studies.

SCHEIDE: There are some techniques available. There is charcoal tube sampling. There are passive badges. These are concentrator devices, and they can be worn very easily.

BACHMAN: I am not sure that they are good for ambient concentrations, however. Certainly they haven't been adequate in ambient samples. Charcoal has been a big problem.

We are not sure that the technology that is useful in the occupational setting immediately translates to the ambient area. The ambient area is a lower order of magnitude in terms of concentration.

SCHEIDE: You are talking about longer sampling times, too.

BACHMAN: That is true.

DR. JOSEPH BREEN: Joe Breen, Office of Toxic Substances. At the lower concentrations, you are getting quantitative recovery samples. But I believe that people are looking at other absorbents that are being used.

DR. JOSEPH BROOKS: Joe Brooks, Monsanto Corporation. I will be reporting tomorrow on the work that we are doing with a combination sorbent collection system. We will be working and looking at 20 carcinogens in a study next year. We are on step right now for validating this sampling system against the 20 carcinogens.

I would say that in certain cases the technology is probably available now. When you say vapor phase organics, you are talking about such a broad range of compounds, and it is going to be a long while before that whole thing is sorted out.

MS. MARY LYNN WOEBKENBERG: Mary Lynn Woebkenberg, NIOSH. We are currently involved in an evaluation program of several sampling techniques. Since you mentioned carcinogens, we are looking at polynuclear aromatics.

We are looking at a mine sampling train which is for particulates and the vapor phase of any PNA's that come through. They are looking at Tenax. We have gotten back one set of samples which will give us approximately 400 data points, which will compare several aspects of the sampling trains.

We are looking at the possibility of using the glass fiber filters and silver membrane filters. We are looking at the need for using the silver membrane filters to see if the Tenax trap behind it will effectively trap all of the vapor phase PNA.

We are looking at various slides in the 37-millimeter cassette 13. We are looking at the 10 cc cyclone. We are also doing a particle size distribution study.

Most of the study that we are doing is taking place in foundry operations, because we know that there does exist a reasonable concentration of polynuclear aromatics after the mold-pouring process and also after shake-out.

So, it is not of the ambient situation, but we are currently doing an evaluation. With the rapid-scanning fluorescence detection that we have available to us, we will be able to look at 18 of the PNA's in relatively short order.

MR. OTTO WHITE: Otto White, Brookhaven Laboratories. Perhaps later on during the course of the evening, I will get a chance to give you some highlights on a project that Brookhaven has been involved in; that is, assessing the industrial hygiene monitoring for the coal conversion oil shale industry. The question of PNA's came up there, and the approach that the committee has recommended in the process of getting the final report in is the use of so-called indicators or proxy compounds--pretty much like SO_2 has been used as an indicator of air pollutants in that the total number of carcinogenic PNA's that are available are so large that you have to settle on looking at 10 or 20 compounds as indicators of the environment's conditions.

MR. DOUGLAS DOCKERY: Doug Dockery, Harvard. I am a little confused. I am trying to understand what personal monitor data have to do with standard setting. I can understand, and I am a little provincial about this, in that we are doing active epidemiological research. I can see where there is a direct need for personal monitoring in terms of health effects research. But in terms of defining how many monitors we need or where they need to be placed, I don't see the utility of that. The only use I see for these devices is in determining health effects.

I would like to know what the motivation is for trying to get these data.

WALLACE: As I mentioned in my paper, of my six uses for the personal monitors, five did not require the health effects measurements. That is, those five uses were simply to gather exposure data for those pollutants, six or seven in number, for which the health effects have already been determined.

The standard setting is affected very strongly by the frequency distribution of exposures, because the standard setting is based on the sensitive portion of the population. If indeed one finds that the sensitive portion of the population is a rather small group that could perhaps be protected by other means, then a serious and strong change might be called for in the standard setting process.

DR. ROBERT CHAPMAN: What other means, Lance, do you have in mind?

WALLACE: Well, for example, there was a paper study by Morgan and Morris that took seven subgroups of the population and estimated their exposures to SO_2, as I recall. Only one of those seven subgroups was found to be anywhere near the level set by the standard. That one subgroup was construction workers who lived in the center of the city and worked outdoors in the daytime. I haven't investigated this, but it does seem possible that respirators or some other sort of individualized protection for them might be a possible alternate reaction to the present approach of setting single, uniform, nationwide standards. However, there could be other possible approaches to the standard-setting process--it could be regional or it could be more closely identified with that portion of the population that may be at risk but for which we have very little data now.

DR. CHIN-I LIN: We are here to talk about personal sensors, and yet we are talking about a very wide spectrum. I wonder if EPA has released some sort of tentative priority list.

WALLACE: I guess one of the problems is we have too many lists. We have a series of lists put out by different offices. And with new information coming in all the time from testing and so on, there is a standard saying around EPA about the "pollutant of the month."

DR. PHILIP WEST: Phil West, Louisiana State University. I admit that I am among those who are confused. Among other things, we see distributed here a list of toxins that are of prime interest. Carbon monoxide appears all the way down through the list. We have heard about carbon monoxide in so many ways. What percent of the population, however, intermittently, almost every day in their lives, are inhaling 300 to 400 parts-per-million of carbon monoxide from the moment they wake up until they go to sleep at night? Why are we worried about the range of 10 to at the most 40 parts-per-million? Why do we say we must have catalytic converters on automobiles, because we can destroy carbon monoxide, when even in tunnels the levels nowhere approach the concentrations that are present in each and every puff of a cigarette?

It seems to me that the priorities are a bit distorted here. We are overlooking things that are much more important, it would seem to me, than something like carbon monoxide.

BACHMAN: The real problem is, you know, whatever people care to do to themselves--quick or slow suicide--in terms of voluntary risks from day-to-day, the general population should be protected from involuntary risks imposed upon them from others and from themselves in their automobiles.

Smoking--I always admit that it is a very real risk that smokers get. While it may not kill them on the spot, it certainly kills a number of them.

To say that many people are exposed to high levels does not say that the lower levels in the ambient area don't cause a real risk and pose a serious threat to the rest of the population.

That is why, indeed, we care about much lower concentrations. Of course, you could use the same argument about people in their occupations, I suppose, who receive much higher concentrations.

Some of the people who don't smoke can also be quite sensitive with respect to carbon monoxide or perhaps other pollutants at lower concentrations. And perhaps if they smoked, they would drop off much faster.

So, the basic premise is philosophy--the will of the people expressed in the Clean Air Act. We can't have people imposing involuntary risks on the general public just because a large percentage of the population--some 30 to 50 percent--is imposing on itself a much, much greater risk.

WALLACE: Perhaps I could continue going down the list of personal monitor priorities expressed by EPA offices.

The mobile sources portion of the air program has a somewhat different interest than the rest of the air program. Of course, they are most interested right now in the diesel question. The automobile manufacturers need a decision some time around the end of 1979 and the early part of 1980 as to health effects of diesel particulates. So, a personal monitor for diesel particulates is one of the high priorities for the mobile sources group.

They have also mentioned nitrogen dioxide, transportation-related pollutants, including lead, and again, the ever-present organics.

Within ORD we have several laboratories that have cited their priorities. The Environmental Sciences and Research Laboratory, which is responsible for development of instrumentation for air pollution measurements, feels rather strongly that the sort of work that we do on personal monitors should build on the work that has already been done; that pretty much limits them to the criteria pollutants. Among the criteria pollutants, they have chosen ozone, with CO as a close second, as their top priorities.

The next list is a list of pollutants selected by our Health Effects Research Laboratory here in Research Triangle Park. However, the list is dated March 1978, and EPA being such a volatile agency, I would be glad to hear anything newer that our HERL representative, Dr. Chapman, has to give us. The old list that we have here is basically the criteria pollutants in a particular order.

CHAPMAN: I am Robert Chapman from EPA. I might say just to start off that I am an epidemiologist concerned at the present time mostly with studies of air pollution in communities as opposed to occupational studies of pollution exposure.

I have been asking myself and some colleagues back at work throughout the conference what is perhaps a more fundamental question than questions that we have all been dealing with up until now (that is from the standpoint of epidemiologists interested in community health effects and air pollution exposure): Where can personal monitors be appropriately used and where can't they be used? I wonder if we could grapple with this question a while?

When I think of health effects of air pollution and other types of pollution, I am inclined to divide them into effects of long-term exposure and effects of short-term exposure. I am having a very difficult time seeing how, from the standpoint of epidemiologists, personal monitors are going to be particularly helpful in our studies of long-term exposure effects.

I would be delighted to be talked out of the way I am thinking right now. But up until now, I have not seen any way in which we would be able to put them to any particularly useful application in such studies, which leaves me with the notion that I think they would probably be most useful--and I am sure that I am not saying anything terribly new--in studies of relatively short-term exposure.

This leads me to a couple of questions, one of which is: From a physiologic standpoint, what kind of averaging time would be most relevant for us to have a personal monitor that would be of any substantial use to us?

It seems to me that the type of monitor that we would be most interested in would be one able to characterize, at the most coarse level, 24-hour average exposures; and considerably finer gradation within that would be useful to us, largely because we really don't have a good handle, as I think some of you think we do, on short-term health effects of the pollutants.

We do have some fairly confident estimates of the types of health effects that are being promoted by pollution exposure, but very, very few available data can be characterized as being solid.

So, the finer the gradation of exposure that we can get a picture of within the day, the better we are going to like it. I would say first that we should have certainly 24-hour average exposures available to us for whatever pollutants we use personal monitors for. I would also say, in my mind and I think in some of my colleagues' minds, that the second most desirable type of exposure averaging time would probably be the daily maximum hourly average within a day. The third most desirable--which is practically equal in my mind to the second--would be some index of the maximum instantaneous concentrations of the pollution in question for each day.

I don't think that exposure times over a period longer than a day without data for shorter exposures are going to be terribly useful to us, to be perfectly honest with you, because of the types of effects or the types of biomedical variables that I can see us measuring in those studies. I don't think it is terribly plausible to think that that kind of variable would be affected by pollution exposures a week ago as opposed to today or yesterday.

I don't really see much point in a big effort being made toward developing monitors whose finest capability is a week-long exposure.

WALLACE: Can I ask about the lead exposure time, which is a month?

CHAPMAN: I would have to admit, Lance, that I am not very good on that. There are a lot of people who can tell you more than I can. I should probably preface what I am saying: I think that what I know best is criteria pollutants--criteria pollutants as they would have been defined up to a year ago.

Yes; you are quite right. I am trying to generalize here. There would certainly be some exceptions. I think, however, that the exceptions as far as I know aren't going to really have me change my mind too much, even though individual ones--other individual ones--might well be thought of.

I have been wondering whether I am right, for example, for a lot of the organic substances. And I must say I am wondering, again from the point of view of a community kind of epidemiologist as opposed to an occupational one, what kind of short-term effects can we hope to see in response to exposure to some of the organics?

I must say I really don't know the answer. I have come up with the question that is rather large in my mind: How helpful to us are the various organic types of personal monitors going to be? I won't say very helpful, and I won't say not very helpful, but I will certainly say that the answer is highly uncertain in my mind. I will have to also say that I can't really come up with a specific application in an epidemiologic study of personal monitors for organics.

I must say that the kind of monitors that I can best get a handle on the use of, a) because I know this kind of pollution best, and b) because I think there may be something to it, too, is the criteria pollutants, again excluding lead.

WALLACE: You raised two questions in my mind, one of which is, among the criteria pollutants, do you have a ranking or do you have studies that are ongoing now that could be improved or enhanced by the addition of personal monitors to those studies?

CHAPMAN: Well, I think there are studies ongoing now for really all of the criteria pollutants, excluding lead, that would be enhanced by appropriate personal monitors. And I must say that I want to stress the word "appropriate."

I am very impressed by a lot of the technology I have seen in the last 2 days, but I have to voice some skepticism as to whether this technology has really received the full gamut of laboratory and field testing that would make us confident of using it.

I say this largely because of assurances that we have gotten over the years of the big instruments--the instruments that are put in ambient situations that are not worn by people. Even these instruments, to my way of thinking, are not entirely debugged as yet.

I think it would be an unrealistic request of any maker of a personal monitor to ask within 2 or even 3 years of the conception of the instrument to have it entirely ready for field use.

I think, on the other hand, that it would not be fair to us epidemiologists to plunge into the field use of such instruments until they were fully verified both in the lab and in the field.

WALLACE: That is a perfectly reasonable request to make. Laboratories within ORD would have the responsibility for evaluating these instruments in the field. I am referring to the environmental monitoring units at our laboratories, either here or at Las Vegas.

CHAPMAN: That is really what I am coming down to, if I could just say another sentence or two. I really can't determine rank within the criteria pollutants, and therefore would be inclined to go along with what I think you said about the ESRL, and that is that I think we would feel the most confident using first the monitor that presently is closest to development. I think we could come up with an interesting and relevant application for it, as long as we were convinced that it was really going to work.

That is more important in my mind than a specific pollutant which is chosen to be measured.

DR. JOHN McSTRAVICK: John McStravick, Energetics Science. You bring up a very interesting point that is something we haven't discussed here in the past 2 days--that is, performance specifications. What are you looking for?

OK. You make a very general statement which I accept. But what kind of accuracy do you need? What kind of configuration do you need? These are the things that we have to get sent back to us as well. I am hoping that this will come out here tonight at the workshop.

CHAPMAN: I think that that is unrealistic. I think this is the kind of thing that we would have to sit down together to discuss for several hours for each substance, really.

WALLACE: John, correct me if I am wrong, but it does seem to me that I remember you or someone at ESI stating that one of the reasons that you developed the 9000 series was because of Anthony Cortese's studies in Boston in which he used the Ecolyzer and stated that he needed something that was more easily portable.

McSTRAVICK: Absolutely.

WALLACE: That seems to me to be an extremely important point, which is that industry will develop the sorts of things for which they are given some indication that there is a need for. And it is, I think, a challenge to EPA to come up with the specifications that we need.

For example, do we need tremendous accuracy in personal monitors for some of the uses we are talking about? I am of the opinion that we do not. We do need sensitivity. We need to go down to ambient levels.

But the sheer number of data points that we can get may make it possible to compensate, by means of a large N, for the fact that they are not as accurate as the large fixed-station monitors.

MEIER: Could I read off something that Joe Behar and I put together last night? We did just what you asked. Don't hold me to what I will read to you as representing all of EPA. This is simply what we at Las Vegas called desirable characteristics. It is quite a long list, but we worked it out among ourselves and thought that we might present it here, which we have not done so, so far.

Let me read some of the things to you, and they kind of answer your questions, I think:

1) Lightweight--light enough to be worn easily by the general public; less than 1 pound, including power supply, is desirable.

2) Durable--able to withstand treatment received by personal equipment such as a wrist watch.

3) Dependable power supply--in our terms, a power supply must be able to provide constant power over a minimum of 24 hours.

4) Easily changed.

5) Tamper proof.

6) No exposed controls that could be easily adjusted by the wearer.

7) Accurate--an accuracy of plus or minus 20 percent at 2 sigma is desired.

8) Sensitive--should be able to detect the parameter of interest at one tenth of the most stringent air quality standard.

9) Sensitive to range of concentration expected in air.

10) Easily calibrated.

11) Separate readout--hourly and daily integrated readings are desired.

12) Reliable--less than 1 failure for 10 units.

13) Free of common interferences--total interferences less than 10 percent of total signal.

14) Traceable to a standard method if possible.

15) Inexpensive--less than $500 per instrument is desired.

16) Stability--capable of operating for a minimum of 24 hours without changing components.

Note that that was just a quick list that we put together.

DOCKERY: I would like to state a different viewpoint from what you were saying about the instruments. We are kind of working at the edge of the science here in trying to measure health effects for new pollutants that are coming along, and things that we have little knowledge about. The instrumentation we are having to use in doing this is really not field tested, hard and fast instrumentation, but instruments that are basically laboratory instruments that we are trying to apply in the field.

We have a lot of failures in going out and trying to use these. I think if you are looking for a market where you are going to go out and sell a lot of these monitors, it doesn't exist. There are going to be a couple of epidemiological studies, and then we are going to go on to something else. I don't think the market exists.

McSTRAVICK: In the industrial workplace, it does exist.

DOCKERY: In the industrial workplace, it does, but not in the ambient environment.

McSTRAVICK: Well, I can address myself to both of them.

MR. DAVID BRAUN: Dave Braun, 3M Company. I am an engineer. I really don't understand or know that much about epidemiological work. But going back to your original idea of short-term and accessible effects that you can look at, it seems to me that with systemic toxins, don't you really want to have a data base for which the time interval is not so important, even if it is a month? Doesn't that fall into the realm of the kind of work you do?

CHAPMAN: Are you talking about things, exposure to which--such as virtually any metal--would be manifestly bad for you?

BRAUN: No, but let's say carcinogens or anything where the long-term effect is important. When you were saying that you really don't see the reason for extended period sampling, I think I would submit that that is one place where--or am I understanding your work incorrectly?

CHAPMAN: No, I don't think so. Let me try and give you some feeling of why I think it is a limited application.

One problem is that we are absolutely proscribed from doing prospective studies in cancer, I think, given both the necessary sample sizes and resources--financial resources--that would be required, even in the best of all possible worlds. Given, at least for us Government researchers, the exigencies involved in launching sustained studies, I think it is unrealistic for a prospective seller of personal monitors, say for carcinogenesis, to launch a heavy research and development program in expectation that scientists in EPA are going to be able to monitor a truly big prospective study--that would be a mistake.

I think it is too bad, but I think it is true. I wish we could do it. But up to now, we are just playing. We have not been able to because of shifting tides that are out of our control.

Another thing that gives me trouble is that I am not really addressing the physiologic part of the question right now. A more scientific than physiologic reservation in my mind is the difficulty of using monitors now to try and determine what exposures have been in the past. Because we are not able to do prospective studies, we are more or less stuck doing retrospective ones; that is, finding pockets, let's say, of high cancer incidence, and then trying to determine in a retrospective fashion what the people have been exposed to.

Now, monitors might be useful to give us an indication of substances in the town now that we didn't really expect were there, or that we thought maybe were there but we didn't know about. But beyond that fact, in a retrospective study--a fact that it seems to me could be turned up with a stationary monitor--a very limited number of stationary monitors may be rotated throughout the town. I really don't know what personal monitors could add. Do you see what I mean?

BRAUN: Yes.

BACHMAN: Let me add something to that, though, because we made a request to put vapor phase organics on the list.

I agree with your comments with respect to epidemiologic studies. We didn't put it on there because we saw a use in epidemiology.

What we see is a use in exposure monitoring, and stationary monitoring is good and useful for this purpose; emissions monitoring is good and necessary, and modeling is going to be used.

In the standard setting with carcinogens, however, it is going to be important to us to have some studies of total body burdens and various exposure regimes to validate our models and to develop better exposure models than we have now.

And we wish to measure what is in the air now so that we can regulate the emissions that are coming out now to prevent future problems--not wait to see the dead bodies 20 years from now.

So, the idea is to get these monitors used in standard settings. So, we do see a use for these instruments, but certainly not in epidemiology.

CHAPMAN: So, you are talking about studies in which there are no specific biomedical measurements?

BACHMAN: That is exactly right. We are assuming a risk of cancer. We can do some extrapolations and get some ideas just from the exposure. This is the use that we see for it.

WEST: First, I swear that I had no input whatsoever to what Gene said a few minutes ago about certain specifications that would be desirable for personal monitoring. He was obviously talking about passive units. And so, three of us in the room right now bless him because he summarized what we would summarize in our talks tomorrow.

I would like to comment on the incremental measurements of hazardous materials. Personally, I have been involved in this work for some 27 years. We started on SO_2 and worked on the acute toxins. These were obvious and spectacular, and people were worried about them. Apparently, we are still worried about them.

I sometimes think that this is in error, because regarding a few toxins, if they don't kill you, don't worry about them. If they do kill you, of course, someone else is going to worry about them.

You have the acute toxins and the cumulative toxins. And there is another group that seems to be overlooked, at least in most classifications--that would be additive toxins. In the case of additive toxins, it doesn't matter very much about how much you get in any one increment. But everything points to an end point at which you have a certain liability that you must pay off.

Concerning radiologic exposures, the same thing applies. You can't backtrack after you have had it. You smoke cigarettes. Now, loosened up by martinis a good many years ago, someone who was very knowledgeable in the industry confessed to me that he knew that a person could smoke one pack of cigarettes a day for 40 years, and there was, say, a 20 percent chance of dying of lung cancer. Or two packs of cigarettes a day for 30 years would give you exactly the same chance. You could have four packs a day for 10 years. You come to the same thing. So, it was strictly additive.

So, if that is the case, then I should think that we would be interested, not in breaking this down to a daily exposure or even a weekly exposure, if we just had the time range averaged for a month for some things. Suppose we say vinyl chloride or benzene.

Now, I don't think that this is necessarily significant as long as it is sublethal. It could be; we don't know. But it could be the additive effect--that is, the total insult from all of these supplemental increments that add up over 5 years or 10 years, or if you don't have very much of it, it may take 30 or 40 years. But somewhere along the line, there is going to be some sort of an accounting.

Now, if that is the case--then some type of monitor that is simple or eloquent in its simplicity--truly I think a passive type monitor is perfectly acceptable, and the accuracies certainly are good. I might add--and I will point this out tomorrow--that we have monitors that will give us a time-weighted average for a 30-day exposure.

I might mention also that we have personal monitors that are passive for tetraethyl and tetraethyl lead that we could easily apply in the ambient atmosphere and have 1 month exposures and get the time-weighted average for that.

So, these are possibilities that I think should be explored. Now, unfortunately, funding agencies have been very parsimonius. We developed a vinyl chloride monitor for $43,000, and we begged and cried to get that.

So, with a little money, I think there is a lot that can be done. But I do think that extended periods are justified in some things.

CHAPMAN: I think that is right. I think it is right for compounds of low concentrations. I might say that I would be delighted to eat the words that I spoke at the outset of my remarks, especially if what we are constantly doing in community health research and air pollutants is associating short-term--say daily or shorter--pollutant exposure with physiologic changes of uncertain significance.

People will cough, for example. Some people may wheeze. Other people may develop eye irritation. We have no real sense that a great many of these symptoms that appear to be reversible are more or less innocuous. We have no sense of the degree to which these are harbingers (after repeated exposures) of some overt disease developing over the long term.

If, with respect to a lot of the compounds, in particular the organics, certain short-term symptomatic or biochemical or hematologic responses could be elicited and tied to the development of some real illness condition down the road, I would be more than happy to take back in a minute what I said before.

One thing that gives me a good deal of trouble, though, is the overuse of scientific energy, or technology development to the exclusion, let's say, of determining what the real meaning of some of these shorter-term responses may be, be they after a month or after a day.

WEST: But not eliminate either one.

CHAPMAN: That is right. Bear in mind the necessity of the concurrent effort.

DR. LARRY LOCKER: Larry Locker, Solid State Sensors. I just want to make the comment that the people who are interested in personal monitoring and selling equipment would like very much to see Government agencies increase the criteria pollutants by hundreds, by thousands. And the instruments that you need--the analytical instruments you need--to get the information that you require, are, I think, quite different from what the prospective market needs.

They want something that is low in cost, light in weight, and which they don't have to change every day. They want something that can be used over a long term. It is only a question of reliability of statistics, the way I see it. For you to get statistics on health effects, you need a different type of instrumentation than would be ideal for someone who wants to monitor in an occupational situation.

CHAPMAN: We certainly want some common features without extreme unobtrusiveness. We just really can't use them in our studies to any particularly good degree. That is every bit as important as the accuracy of the instrument.

Maybe I shouldn't say this since by doing so I am pointing out the limitations in our field. But I am inclined to agree with you, Lance, that extreme accuracy isn't all that important. My first reaction is that the precision of instruments, reproducibility of response from one instrument to another, may be more important for us than very delicate accuracy.

DR. EDWARD McMADDEN: Ed McMadden, Gastek. As a manufacturer, I guess I can say in all honesty that we are quite pleased with the possibility of EPA's getting into this kind of instrumentation.

But we seem to be talking a great deal about organics. I don't believe there would be a challenge if I were to say that within the criteria that were set down, which include hourly accumulation, that there is nothing presently in the wind other than 24 badges which are changed on the hour at the stroke of the clock which are going to do that job for organics.

Rather than spending a lot of time chasing off on that tangent, it appears that within the criteria pollutants--although the instrumentation available right now does not meet all your specifications--in CO, it is quite close. Out of our total of 16 entries for pollutants to be measured, CO constitutes a quarter of those. The same basic type of technique can be used to measure another group of the nitrogen oxides, sulfur dioxide, and so forth.

So, that takes care of a total of half the entries. Can we now eliminate some of the things that probably are at best well beyond the horizon at the present time and concentrate particularly on CO because we could have something reasonable with the technology that is available now?

I am not sure that your $500 criteria will be met. But be that as it may, what numbers are we talking about? Are we talking about dozens? Are we talking about hundreds or thousands?

This will be helpful to us if we can get specific and right down to the point where we are close today as manufacturers.

WALLACE: Two comments in response to that. One is that that is a fair question about the numbers. I can probably give you some response to that. The other is that we really have two areas involved here. First, we have studies that we could do almost immediately with existing (properly evaluated) instruments. Secondly, we look into the future and decide what we need to develop for the next few years or the next dozen years or so. And there, we do have to look beyond what is available now.

BACHMAN: I am afraid there is a misconception here. There are several kinds of needs. Chad was talking about epidemiological needs. When he says an hour, that is one thing, and it is useful in that short-term system. You are asking for organic monitoring, and I think CTS and the others on the list--by the way, there are four CO entries and four organic entries--anyway, the other people are also asking for organic measurements. They are talking about the same kinds of problems we are: carcinogens and these long-term effects. What you are talking about is apropos, and maybe we are not so far over the horizon. That is important to us. But I think it is a real need you will have. A number of people are obviously interested in it. So, I don't want to turn off anybody.

McMADDEN: I am not trying to down play organics. What I am saying is that we have in one area an approach that is reasonably close to your desires. What I am saying is that if this group cannot come up with some sort of meeting of minds where we are close, I think it will be less productive to get driven off on other things which really are much further away.

Granted, that for the long term, it is useful. But for manufacturers, that would be another thing.

MAGE: I would like to ask Otto White if he wouldn't mind briefing us on what was discussed at Brookhaven. I think maybe some of the very same questions have been handled there, and perhaps it would be beneficial for us to get this input from their point of view.

WHITE: Brookhaven was asked by the Department of Energy to assess the industrial hygiene monitoring needs of coal conversion in the oil shale industry.

The way we attacked that was to formulate what we interpreted to be an authoritative group, consisting of names within the field of industrial hygiene. The committee met three times. The final meeting concluded with a symposium similar to this, in which the theme of the first day was to identify the industrial hygiene monitoring problems for the emerging possible field industries. On the second day, the theme was to address the state of the technology for performing these monitoring needs.

We identified at that time a number of monitoring needs for the occupational environment. They include things like the evaluation of health effects, monitoring performance of engineering controls, monitoring trends within those controls, developing designed requirements for doing the controls, documentation of exposure levels, testing for compliance purposes, measuring process losses, selection of suitable respiratory detector devices, identification of contamination sources, and assessing emergency conditions.

When we started attacking the problem, one of the things that turned out to be extremely important were the polysaccharide hydrocarbons. If you look at the process characterization--the effluent characterization studies--you find some thousand compounds for which toxicological studies indicate that some neoplastic or carcinogenic properties are associated.

We also associated the industries with their use of some very common materials, a number of which appear on your list.

So, the first thing the working crew did was to categorize the hazardous potentials of some of these materials. We developed four categories: the first was materials immediately hazardous to life and health. The second category was high risk but not immediately hazardous. The third was a moderate risk, but not highly hazardous. Fourth was short-term, nonroutine, high hazard conditions.

We had to ask ourselves some questions. The questions that required answering were: What compounds were present in each hazard category class? Is the monitoring technology currently available for that particular pollutant? Is the current technology compatible with future needs? If not, is technology being developed to meet that projected need, and when is the technology needed?

In the high hazard category we listed six compounds, hydrogen sulfide, carbon monoxide, the oxides of nitrogen, oxygen deficiency, and coal and shale dust, as well as hydrogen.

We said these materials were present in such concentrations within these processes that acute irreversible effects could result from exposure. The working group believed that the technology was available to provide equipment which could be used as personal and area monitors for continuous and direct reading and long capabilities for hydrogen sulfide, carbon monoxide, oxygen, and hydrogen, of course.

However, the technology was lacking for monitoring exposure levels of coal dust and nitrogen oxides in a format that would give the personal capability. We also did not believe that these six substances were unique for the coal conversion oil shale industry. So, this particular group recognized no special priority from this standpoint for these particular forms of instrumentation.

The second category that we looked at was the high risk but not immediately hazardous category. We classified within this category materials which cause irreversible effects but were not present in sufficient quantities to produce acute toxicological effects. The carcinogenic, mutagenic, and teratogenic organics are included in this group, as well as some of the trace metals, dust, and fibers.

I don't think it would be fair to you to read through the draft of the report, but I will point out some of the specific research suggestions that the committee will be recommending to the Department of Energy.

In terms of personal monitors for gases, the working group encouraged that there be additional evaluation of current instrumentation under various conditions of interference, temperature, pressure, humidity, etc., to ascertain the appropriateness for future needs.

It is likely that passive monitors will remain a primary monitoring tool. Improvements needed include the development of a new substrate to expand the diversity of measurable compounds and to allow higher flow rates.

We believe that this area is likely to provide high payoff in a few years.

We also recognized the need to increase personal monitoring pump flow rates.

And that has been identified as one requirement for obtaining sufficient samples to facilitate bioassay samples.

Both benzene-soluble fraction and benzo(alpha)pyrene have been recognized as potential indicators in the coal conversion industries. There appear to be some drawbacks in use of these particular tools as monitors in that you need a little more material to run your sample than is currently available, say, for dust samples.

So, we recognized that you need to have personal-type pumps, similar to the MSA Model G. The committee looked at second generation instrumentation.

The working group encouraged the development of new sampling instruments which will facilitate automatic analysis and data recording to permit the handling of large amounts of data. And the working group therefore encouraged the development of the personal gas chromatograph. The Stanford research group has a pocket-sized gas chromatograph which can monitor some 10 compounds and give you a time-weighted average or the cumulative concentration or dose at the end.

We would encourage this type of instrumentation, which presently has been funded by NIOSH, but DOE should look at this for the polysaccharide hydrocarbons which may require another type of detector and maybe some different substrates in terms of the column.

Additionally, we felt that real time data reporting is necessary only for the Class A compounds; that is, the carbon monoxide, hydrogen sulfide, and those immediately hazardous compounds. We felt that in other cases, the most attractive approach is a personal sampler, which either can report results of real time analysis over the course of a day or collect a sample over the course of a day, and at the end of the day the sample is inserted into a device which either analyzes or records the exposure automatically.

We also found that there is a need for looking at nitrogen compounds. There are no good sampling techniques for ammonia and hydrogen cyanides, as well as nitrogen, which are of particular interest in the oil shale industry.

In the area of aerosols, our comment here is that this is an area where there are many needs, but that it is one that does not appear to be right for exploration. For example, there is a need to do in situ chemical characterizations, with no avenues for research in this area being evident, and a size cutoff at 15 microns and 2 microns, consistent with the recent EPA finding should be made. Current technology is adequate for this, and development of more sophisticated devices is not recommended at this time.

We believe that in terms of particle or aerosol monitoring, we need to: improve the efficiency of collection; improve the extraction efficiency for the separation techniques, chemical specification, and in situ separation of soluble and insoluble particulates; and to review the state-of-the-art used for personal particulate samples to determine their needs in the future research.

In the area of metals, we identified possibly five metals of concern. They include arsenic, cadmium, chromium, and nickel. Lead was not included in our particular list.

However, we are concerned that the toxicity of metals varies with their biological availability. A classic example is chromium, and also chemical compounds. Our current technology does not provide insights on these factors, and research is needed to provide this additional information.

One area of exposure in terms of these new industries is the contamination of surfaces--that neither are there safe permissible levels for skin contamination, nor are there good techniques for evaluating skin contamination. We recognized a need in that area.

One area where the committee wanted to provide some insight was in analytical development. We thought that we should encourage the refinement of analytical tools and techniques for materials which are identified by those characterization studies--that is, process streams and air pollutant characterizations. But we did not believe that it would be appropriate at that time to dilute the available funds to develop a few high technology devices. There are a number of papers on the Auger spectrometer. We thought that that wasn't the particular analytical device that would receive funding in other areas.

Basically, that summarizes the committee's concern. We felt that personal monitoring had its place. We were concerned that these industries were going to be approximately 1 square mile in terms of area. The use of area monitors probably should be evaluated. But certainly for operations similar to all refinery-type operations, personnel monitoring is probably going to be one of the major tools.

It is interesting to find that some of the compounds that we are concerned with are compounds that EPA is concerned with in the environment.

MAGE: Thank you, Otto. In your view, as a representative of the committee, did it also envision personal health monitoring and personal exposure monitoring simultaneously?

WHITE: The area of personal health monitoring was not really addressed by the committee. The committee was concerned about a time some 20 years from now, having a Mancuso-type concern in terms of this particular industry. And so, the need to get a handle on all the parameters that are available is paramount. We did not address the physiological monitoring question; no.

MAGE: I would just like to say that we are thinking of epidemiological studies of a thousand subjects and a thousand personal monitors, and that is not the only use of the personal monitor.

Everybody knows that there are economic considerations involved in setting air quality standards and regulations. We have just witnessed the Automobile Manufacturers Association's ability to get a relaxation of our standards on vehicle emissions set back year after year. These are economic considerations.

One of the economic considerations that we have to take into account is the number of people who are exposed to particular pollution levels. We are setting standards which are required to be met by the States through implementation plans. The States have to reduce emissions in order to bring air pollution down below the standards.

It is going to be very important for us to prove that not only are those measurements representative of communities, but indeed that there are a significant number of people who are exposed. Also, we will have to answer the question: "Are the effects of in-home and nonambient environments more pertinent for us to worry about than the 1 or 2 hours of ambient exposure that we might have outdoors?

So, there are many reasons why we should look at personal monitors other than for the purpose of conducting epidemiological studies.

I look forward to the day that the personal physiological monitors are inexpensive, handy, and reliable, so that we could put one out with each personal exposure monitor.

But I think until that day comes, I still see a use for personal exposure monitors simply for characterization of exposure, if for nothing else.

WALLACE: All it requires is a redefinition of the word ambient, or rather, going back to what it originally meant, which was surroundings--the air that surrounds you in the vehicle and the home is ambient air.

DR. VIC SOCOL: I think we have a basic question here. I think we have the manufacturer represented and the scientific community represented. Who is going to lead the way? Is the manufacturer going to establish what he can build, the criteria that he can build it to, and tell the scientific community, "This is what we can do"? Or is EPA or the scientific community going to tell the manufacturer what is wanted both qualitatively and quantitively?

It is the question of the cart leading the horse or the horse leading the cart.

WALLACE: I think it is exactly that question.

SOCOL: That is what I hope will come out of this whole meeting.

WALLACE: Yes. We have one manufacturer asking to tell him what our plans are. I think that it is the sort of challenge that we ought to try to meet. In response, you can tell us whether we are off target, and perhaps we can come together.

SOCOL: I think a manufacturer can do whatever the scientific community requires him to do, although not necessarily at the cost that you have stated. It is a question of numbers. It is a question of cost. It is a question of what you really need.

DR. GEORGE MALINDZAK: George Malindzak from Ohio. I represent another level of confusion, in that I presume that the majority of the group is talking about personal exposure monitors. I represent those individuals who are concerned with the physiologic monitors.

My confusion is associated with the realistic need for collecting personal exposure information in the absence of the physiologic consequences. Where does that get you? I don't understand the purpose of putting all this effort in collecting exposure information if you don't understand what the human response is going to be.

WALLACE: There are two possible answers: one is that it is expensive to collect extra information on health effects along with exposure; and the second is that if you already have established health effects for given levels of the criteria pollutants, then the exposure measurements satisfy certain other needs and thus should be extended.

For some noncriteria pollutants, such as carcinogens, there may be some purpose in collecting exposure information without concurrent physiological responses, since they have already been shown to be carcinogenic in some clinical or toxicological way.

I am not trying to say we should not collect physiological evidence. I am in fact in favor of that. There are questions of funds that have to be considered also.

MALINDZAK: Technologically, it is probably simpler to collect physiological information than exposure information.

WALLACE: There is also a factor of ignorance of the possibilities of collecting physiological information on the part of the people who are in the air pollution field, in many cases. I certainly speak for myself about not knowing what is possible and what is not possible in that area.

I would really be anxious for the insights of the physiological contingent to be brought forward.

DR. THOMAS FEAGANS: Tom Feagans, EPA. I would like to support Lance and Dave in their thought that this second kind of information on personal exposure would be very valuable to us in OAQPS. Whatever your level of knowledge about health effects of a given pollutant, it helps us to estimate what the consequence of various possible standards we might set would be, no matter what the exposure levels would be.

MAGE: Even though I believe that the Clean Air Act says that the Administrator of EPA is supposed to set the standard irrespective of economics, I might say that economics do play a role. It is a significant question.

Now, in order to evaluate the economic effect, which of course is in units of millions of dollars, we have to know what level of exposure the general public receives, and we have to know, if we set a standard, how many people we are protecting.

Thus, even though we may not be measuring the health effect directly in an epidemiologic study, it doesn't preclude the need to measure the exposure.

On the other hand, we have to recognize that our standards are living standards. They are not dead and fixed in concrete. The Clean Air Act requires us--mandates us--to review our standards every 5 years at a minimum, and the Administrator can change a standard at any time that he feels there is new evidence to justify it.

There is a long-range payoff for control of air pollution or relaxation of standards if you can justify it, so that it does justify expenditures of millions of dollars in order to save billions. But it is hard to get those millions.

I think that it will be very beneficial that we are doing the development work on the personal physiological monitors, because I don't think that the last epidemiological study has been done yet.

CHAPMAN: I certainly hope not.

SCHEIDE: I have one comment. We have to keep in mind why we monitor. The reason we monitor is to identify problems. Whether the action level is set low or high is another question that Government organizations have to deal with. No matter where it is set, we still need to monitor to identify problems. That is what we have to keep in mind.

MALINDZAK: But a problem represents the differential between what you expect and what you find. If you never look at the physiologic information, you are never going to change that standard with respect to physiologic consequences. If you are going to devote all your effort to exposure monitors, you are never going to change the physiologic consequence which you learn to establish the standard to begin with.

My point is that there is a maldistribution of effort; that all the effort seems to be going into the exposure monitor. If you want to characterize the population exposure, you don't need personal monitors. You very well should have fixed stations.

But the object is to characterize the physiologic response to this exposure, not just to collect exposure information.

FEAGANS: I agree with one point you made, but disagree with another. I agree with the point that personal monitors can certainly play a role in epidemiological studies to help us learn more about what patterns of exposure cause what effects.

But I don't agree with the second point about a stationary monitoring network being sufficient to tell us all we need to know about those patterns to make the estimates that I mentioned the last time I spoke.

MALINDZAK: I said if you want to characterize the exposure of population, you don't need personal monitors. The purpose was to characterize the population exposure, not to know all about the exposure of that population.

FEAGANS: But I think the personal monitors give you a finer grade of characterization that is very helpful to us in making the estimates we need to make.

MALINDZAK: There is no question about that. I don't argue with that at all.

McKINNON: Not only a finer grade. I think it is necessary to characterize the exposure initially. I think several people in the room will agree that the air monitoring that is done in fixed sites certainly doesn't account for a lot of population factors that determine exposures, even in groups with large numbers of people.

MALINDZAK: I would like to make the record clear. I support personal monitors, but for different reasons. I support your personal physiologic monitors to run concurrently with exposure monitors so that the response to these exposures can be characterized in a realistic and scientific manner, so that we can respond to them in an intelligent way.

Right now we don't collect the physiologic information concurrently with exposure.

MAGE: Another reason for the use of physiological monitors is that we must, as an agency, keep progressing the state-of-the-art. We are running clinical studies in parallel with epidemiological studies. We are doing new and different things. We are discovering new things all the time.

A colleague of mine told me that there are some 8,000 medical journals published throughout the world on all aspects of medicine. It is very possible and very probable, that somebody is submitting for publication right now, in some place in the world, something which will define a heretofore unobserved physiological effect.

Suddenly we are going to have thrust upon us a request to replicate that study or a need to go out and monitor. If these personal physiological monitors aren't being developed parallel with all our thrusts in epidemiology, in clinical studies, and personal exposure, we might find ourselves again with our pants down, 3 years behind, simply because we didn't have the foresight to recognize that although there might not be some kind of acute symptom that we can see from the outside, perhaps some of the devices that George and Matt developed could see from the inside, and had we spent the money, we might have had those devices.

So, we need people who are looking ahead in the same way that we need people who are looking today, to keep our feet on the ground. We need these people who know the state-of-the-art of the developing technology, who see the abilities of micro circuits and also know the physiology, and who can say, "This is a possibility." Then, it will be here when we need it.

Although it might be impractical at the moment to put a thousand of these new devices out with a thousand subjects in a particular health study, we can't simply say we don't need it.

I think we need both long-term and short-term research.

I have now heard about eight or nine Government agencies who are working in this area and not all of them are talking to each other. We have EPA, NIOSH, the Departments of the Interior, Commerce, and Energy; all kinds of agencies. There should be some kind of coordinated plan. Perhaps Congressman Brown's idea, of a bill which would establish a monitoring program, would provide a mechanism for long-range research as well as short-range development.

Even though there is no immediate payoff from development of personal physiological monitors in epidemiological studies scheduled for this year, I think we should make certain people in the Government agencies recognize that it is something that we definitely need in the future.

I can't imagine our not needing it in the future, as our ability to see inside the human body progresses.

SOCOL: I would like to change some of the things that I was going to say based on what Dave Mage said.

When you go into personal monitoring and physiological monitoring, the effect is going to be different on me--who weighs 130 pounds--than on a man who weighs 180 to 200 pounds. It is going to be different on a child and different on an adult. It is going to be different by age. It is going to be different by sex.

I feel that personal monitoring is going to become more effective than fixed-station monitoring, where you don't know what effect you are getting on what particular individual. I think that you can achieve more physiological information by the personal method than by the fixed method.

I am borrowing from what Dave has said to respond to your remarks.

WALLACE: OK, thank you very much.

A New Personal Organic Vapor Monitor with In Situ Sample Elution

Donald W. Gosselink, Ph.D., David L. Braun, Haskell E. Mullins, and
Sandra T. Rodriguez
Occupational Health and Safety Products Division
3M Company
St. Paul, Minnesota

INTRODUCTION

In considering a new approach to monitoring personal exposures to organic vapors, the steps in an overall monitoring program can be individually addressed:

1) Development of monitoring plan
2) Purchase of supplies
3) Preparation of equipment
4) Sampling of personal exposures (includes recording data during sampling)
5) Preparation of sample for analysis
6) Analysis and TWA calculation
7) Report communication and follow-through.

In examining and improving current methods for carrying out each of the above operations, we have evolved a monitoring system which simplifies the work while maintaining desirable objectives and monitoring requirements. The monitoring system which evolved is the 3M Brand Organic Vapor Monitor No. 3500 (see Figure 1).

We can now consider the way in which this monitor interacts in each of the above seven areas.

Step one, monitoring planning, is simplified because the 3500 system allows the hygienist to work through trained aides in remote locations. It also helps increase the number of samples taken in the case where the hygienist

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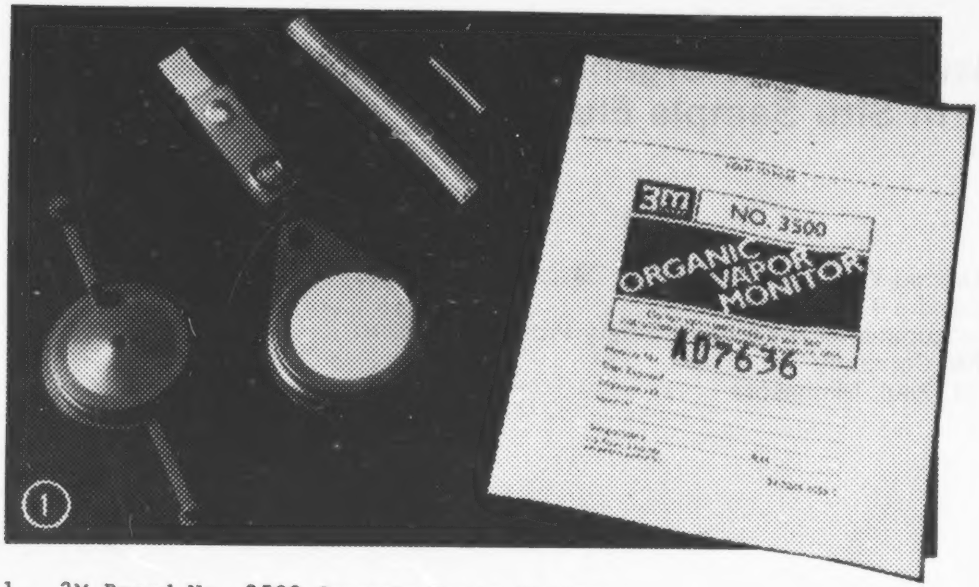
①
3M
NO. 3500
ORGANIC VAPOR MONITOR
A07636

FIGURE 1. 3M Brand No. 3500 Organic Vapor Monitor.

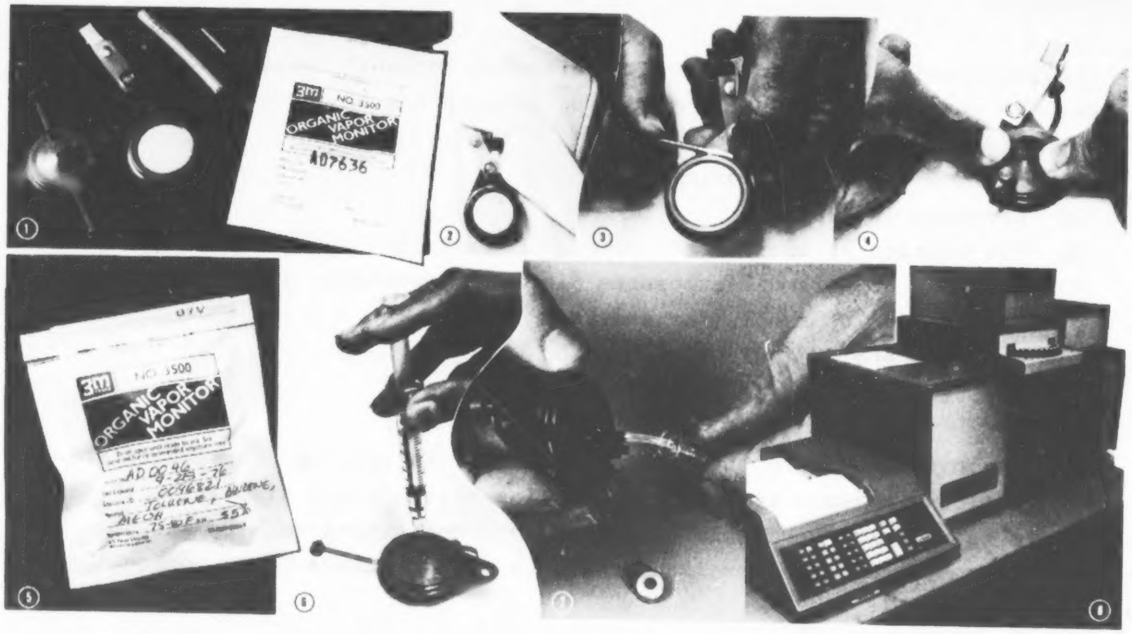
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FIGURE 2. Use instructions for the 3M Brand No. 3500 Organic Vapor Monitor. (The numbers in the illustration refer to the steps outlined in the text.)

is present for the monitoring, thereby lowering hygienist cost-per-sample. Purchase of supplies, step two, is reduced, since only a single product is needed. Step three is virtually eliminated, because the 3500 monitor needs no preparation or calibration by the user.

In the conduct of step four, or the actual exposure sampling, the monitor is readily accepted by employees wearing it. Monitors are individually identified, and the exposure time is recorded directly on the monitor. The package can be used to record comments and other data. A cap terminates sampling and hermetically seals the sample.

Sorbent transfers and other analytical preparations normally comprising step five are eliminated because the capped monitor is already a discrete sample ready for elution. Step six, the actual analysis, is aided by in situ elution of the contaminants from the sorbent. Manual or automatic gas chromatographic analysis is also facilitated by the monitor design.

Efforts in preparation of reports, step seven, are reduced by having all the needed information concerning the sampling on the monitor package for calculation and reporting. In the next section, the objective is to technically describe the 3500 system.

PRODUCT DESCRIPTION

A pictoral representation of the monitoring and analysis method using the 3M Brand No. 3500 Organic Vapor Monitor is shown in Figure 2. Referring to the numbered steps as illustrated:

1) The monitor is removed from the package. Exposure start time is recorded on the back of the monitor.

2) The monitor is attached near the breathing zone of the worker. After exposure, the exposure end time is recorded on the back of the monitor.

3) The white face of the monitor is removed.

4) The elutriation cap is snapped on, and the ports are sealed.

5) The sampling information is recorded on a package, and the monitor is inserted. The package is sealed with the tubular closure.

6) The eluent is added through the center port, and the port is immediately resealed.

7) After 1/2 hour (with occasional gentle agitation), the eluent is decanted into the sampler vial, or an aliquot is removed from the center port for manual injection.

8) The gas chromatographic sample analysis is carried out by conventional means.

The time-weighted exposure level is then calculated using the following equations:

$$\text{mg/m}^3 = \frac{\text{Corrected weight on monitor (nanograms)}}{\text{Sampling rate (cm}^3\text{/min) x sampling time (min)}}$$

$$\text{ppm} = \frac{\text{mg}}{\text{m}^3} \times \frac{22.4\text{/mole}}{\text{m.w.g/mole}} \times \frac{\text{T° K}}{273\text{° K}} \times \frac{760 \text{ mm Hg}}{\text{Pmm Hg}}$$

The corrected weight on the monitor is obtained from the sample analysis after corrections are made for blank samples and desorption efficiency. The sampling rate for each contaminant is determined and published by 3M Company, as discussed in the next section.

PRINCIPLES OF OPERATION

Diffusion Equation

The relationship between environmental contaminant concentration and the weight of material collected by the monitor is given by Equation 1:

$$M = D\frac{A}{L}Ct \qquad [1]$$

where M = total mass of contaminant collect (nanograms)
D = molecular diffusion coefficient (cm^2/sec)
A = diffusion path area (cm^2)
L = diffusion path length (cm)
C = environmental contaminant concentration ($\text{mg/m}^3 = \text{ng/cm}^3$)
t = sampling time (sec).

Equation 1 assumes that the contaminant concentration at the face of the monitor closely approximates the environmental concentration, that the monitor wall effects are negligible, and that the collection efficiency of the sorbent element is unity.

In normal use, environmental concentration (C) is to be determined, mass collected (M) is determined via gas chromatography, and the monitoring time (t) is measured. Therefore, a value for the $D\frac{A}{L}$ term is needed to solve the equation. Substitution of the appropriate units for D, A, and L reduces to cm^3/sec units, which defines the sampling rate for the contaminant and shows the correspondence between diffusion-controlled monitors and conventional pump methods. The diffusion-controlled monitors do, in effect, sample the contaminants in air at a useful, calculable rate. The driving force for sampling is the concentration gradient between the collection face and the sorbent layer in the monitor.

Monitor Calibration

Parameters Calibrated. Monitor calibration data are provided by 3M Company for many organic vapors of industrial hygiene importance. The items which are provided are:

- Sampling rate ($D\frac{A}{L}$ from equation)
- Recovery coefficient
- Exposure limit
- Environmental effects
- Sample storage recommendations
- Concise equations for calculation of results.

Calibration Apparatus. Monitor calibration requires that accurately known exposures be made. Typical equipment for generating known, time-weighted, average contaminant concentrations is shown in Figure 3.

The compressed air from the gas cylinder is passed through a charcoal bed to remove any organic material which may be present. The air flow is integrated by a calibrated flow meter. The organic liquid to be studied is placed in the bottom of the diffusion column, which is divided as shown by a porous membrane. The organic vapor diffuses into the dilution air stream at a calculable rate, and a wide range of contaminant concentrations are attainable by varying diffusion column diameter and length, dilution air flow rate, or diffusion column temperature. The monitor exposure section is a metal conduit with a series of ports into which monitors fit snugly. The design permits easy exposure replication to give good estimates of monitor precision. A simple insert makes adaptation to charcoal tubes possible for comparison studies. The air stream finally enters a large collection chamber where the relative humidity is monitored and the contaminant concentration verified with a calibrated hydrocarbon analyzer. The monitors exposed in series each removes a small fraction of the contaminant (usually less than 0.5 percent), but the amount removed is calculable, and corrections are easily made. The dilution air stream can be humidified by several means between the flow meter and diffusion column.

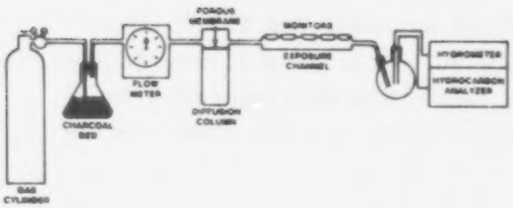
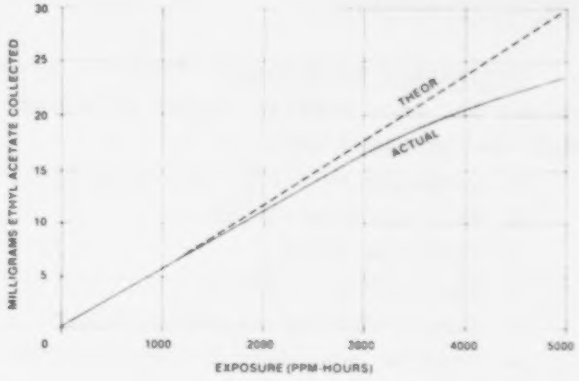
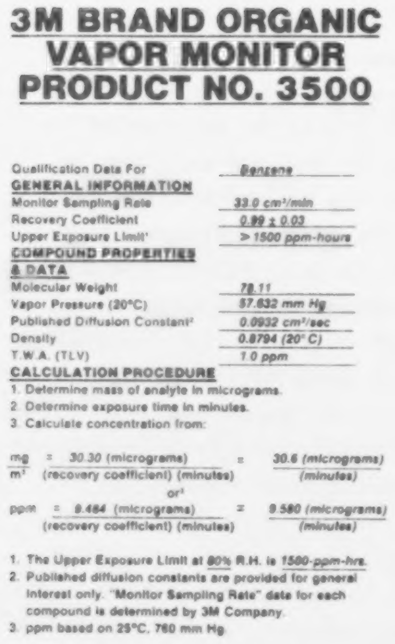

POROUS MEMBRANE
MONITORS
EXPOSURE CHANNEL
HYGROMETER
HYDROCARBON ANALYZER
FLOW METER
DIFFUSION COLUMN
CHARCOAL BED
GAS CYLINDER

FIGURE 3 (left). Monitor calibration apparatus.

FIGURE 4 (right). Ethyl acetate exposure limit.





3M BRAND ORGANIC VAPOR MONITOR PRODUCT NO. 3500

Qualification Data For	*Benzene*
GENERAL INFORMATION	
Monitor Sampling Rate	*33.0 cm³/min*
Recovery Coefficient	*0.99 ± 0.03*
Upper Exposure Limit[1]	*> 1500 ppm-hours*
COMPOUND PROPERTIES & DATA	
Molecular Weight	*78.11*
Vapor Pressure (20°C)	*57.632 mm Hg*
Published Diffusion Constant[2]	*0.0932 cm²/sec*
Density	*0.8794 (20° C)*
T.W.A. (TLV)	*1.0 ppm*

CALCULATION PROCEDURE

1. Determine mass of analyte in micrograms.
2. Determine exposure time in minutes.
3. Calculate concentration from:

$$\frac{mg}{m^3} = \frac{30.30\ (\text{micrograms})}{(\text{recovery coefficient})\ (\text{minutes})} = \frac{30.6\ (\text{micrograms})}{(\text{minutes})}$$

or[3]

$$ppm = \frac{9.484\ (\text{micrograms})}{(\text{recovery coefficient})\ (\text{minutes})} = \frac{9.580\ (\text{micrograms})}{(\text{minutes})}$$

1. The Upper Exposure Limit at 80% R.H. is 1500-ppm-hrs.
2. Published diffusion constants are provided for general interest only. "Monitor Sampling Rate" data for each compound is determined by 3M Company.
3. ppm based on 25°C, 760 mm Hg.

FIGURE 5 (above). 3M Brand Organic Vapor Monitor representative qualification sheet.

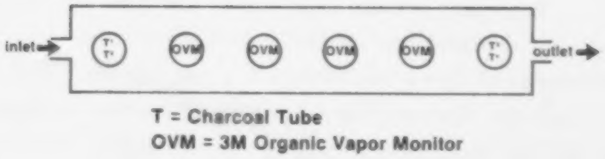

inlet
T¹ T²
OVM
OVM
OVM
OVM
T¹ T²
outlet
T = Charcoal Tube
OVM = 3M Organic Vapor Monitor

FIGURE 6 (above). Sampling sequence gasoline exposure.

When a substantial amount of liquid is introduced into the diffusion column, the system is capable of equilibrating to generate stable, known concentration environments for long periods of time. More typically, a known quantity of organic liquid is added into the diffusion column and allowed to evaporate to depletion as indicated by the hydrocarbon analyzer. Using this method, an accurate time-weighted average contaminant concentration can be determined by only two measurements; a gravimetric weight determination of organic liquid (mg) and a calibrated flow meter reading (m^3). As the organic liquid evaporates, the concentration varies with time, but the time-weighted average concentration is known at the end of the experiment. Both diffusion-controlled monitors and pump methods are capable of integrating variable concentration, so this factor is of no consequence.

Calibration Techniques:

1) Sampling rate

The sampling rate of the 3M Organic Vapor Monitor is determined experimentally by generating known concentrations of each contaminant, exposing and analyzing the monitors, and solving Equation 1 for the $D\frac{A}{L}$ term. The published sampling rate is generally based on three separate determinations in the 0.25-2 TLV, 8-hour exposure range. This experimental determination is considered necessary since desired diffusion coefficients (1,2) are not always available, and their accuracy is not usually known.

2) Recovery coefficient

The recovery coefficient is determined by vapor-state spiking of monitors. This is accomplished by removing the white barrier film of the monitor, placing a filter paper on the diffusion spacer plate, snapping on the elutriation cap, and injecting a known quantity of the organic material onto the filter paper through the center port. The monitor is aged 16 to 24 hours before elution to allow total transfer of the organic material from the filter paper to the sorbent. The published number represents the mean ± 2 standard deviations from the tests conducted by 3M. It is, however, recommended that recovery coefficients be at least verified by the user, since techniques and presence of multiple contaminants can affect recovery coefficients.

3) Exposure limit

The capacity of the monitor for each individual compound is based on molecular structure, vapor pressure, environmental conditions, etc. The exposure limit is specified in lieu of a need for a "back-up" section. This is done by 3M by plotting the weight of the contaminant collected by the monitor versus exposure. (See Figure 4.)

The exposure limit is specified as the weight of contaminant collected when significant deviation from linear adsorption is noted. For strongly adsorbed materials, this limit is usually of the order of 15 mg.

4) Environmental effect
The ultimate vapor capacity of the monitor is sometimes affected by relative humidity. The exposure limit test described above is repeated at 80 + percent relative humidity, and deviations due to relative humidity are noted.

5) Sample storage
Monitor samples which have received duplicate exposures are stored and analyzed after 1, 7, and 14 days. If deviations are noted, refrigerated storage is recommended.

Overall information and recommendations are published on qualification sheets. Figure 5 shows a representative qualification sheet for benzene.

PRODUCT USE DATA

Benzene Monitoring

Using equipment as pictured in Figure 3, known benzene vapor concentrations were generated in air and monitored using the published benzene sampling rate (33.0 cm^3/min). The analytical procedures outlined in the "Product Description" section were followed. Table I is a summary of results comparing the 3M Organic Vapor Monitor to the known generated benzene concentrations. Tabulated values for the 3M monitor represent the mean of four separate determinations ± 2 standard deviations. The values fall well within the accuracy requirements contained in the OSHA standard.

Complex Mixture Analysis

It is recognized that in real field-monitoring situations, combinations of organic vapor contaminants are typical, and that any feasible monitoring system must be capable of complex mixture analysis.

Gasoline was used to test the capability of the 3M Organic Vapor Monitor to sample complex hydrocarbon mixtures. It was reasoned that the high boiling components of gasoline would not be present during a typical exposure. To simulate a more likely field situation, a fraction of gasoline was distilled

TABLE 1

Benzene Monitoring Test

3M ORGANIC VAPOR MONITOR VS. TEST CONCENTRATIONS

Test Concentration (ppm)	3M Monitor No. 3500 Measurement (ppm ± 2σ)
7.80	7.75 ± 0.43
4.13	4.12 ± 0.23
2.27	2.22 ± 0.06
1.32	1.23 ± 0.04
0.99	0.91 ± 0.06

TABLE 2

Results of Gasoline Exposure Test

Components of Gasoline	Test Concentration (PPM)	3M No. 3500 Concentration (PPM ± 2σ)	Charcoal Tube Concentration (PPM ± 2σ)
Pentane	5.602	5.832 ±.408	5.053 ± .500
Heptane	0.573	0.570 ± .045	0.578 ± .082
Octane	0.294	0.307 ± .047	0.329 ± .056
Benzene	0.928	0.892 ± .160	0.873 ± .180
Toluene	1.768	1.710 ± .119	1.552 ± .220
Xylenes	1.153	1.230 ± .086	1.034 ± .160

TABLE 3

Integration of Variable Concentration

1.3 Butadiene Generated Concentration (PPM)		3M No. 3500 Concentration (PPM ± 2σ)	Charcoal Tube Concentration (PPM ± 2σ)
528		527 ± 44	546 ± 78
1585		1690 ± 74	1687 ± 127
3170		3502 ± 223	3489 ± 179

from a bulk sample. The fraction used was the first 80 percent of distillate collected. The remaining 20 percent was discarded. A syringe was used to inject 1.24529 grams of the light fraction through a septum capped port into a receiving vial. An air flow rate of 9.1924 liters-per-minute was allowed to pass over the open vial until all the gasoline had evaporated into the air stream. At the conclusion of the test, the total air volume was determined by the change in readings of a Model 175-S Rockwell flow meter. A total of 11.581 cubic meters of air had passed during the 21 hours required for the gasoline distillate to evaporate. A flame ionization detector was used to verify the test end-point. Charcoal tubes were used to collect samples for comparison and correlation of test data. The tubes and 3M monitors were randomly selected but placed in a set pattern on a sampling channel. Two charcoal tubes were placed side-by-side in the first sampling port, followed by four 3M monitors in ports two through five. Port six contained two more charcoal tubes, again placed side-by-side (see Figure 6).

The charcoal tubes were positioned vertically to prevent channeling, and the 3M monitors were positioned so that the air stream would be flowing parallel to the face of the monitor at approximately 100 fpm air velocity. One and one-half milliliters of spectroquality carbon disulfide were used to desorb the collected gasoline vapors. The samples were allowed to set for 30 minutes with occasional agitation, and were then transferred to a vial. Withdrawal of a 2 microliter aliquot from the sampling vial, and injection into a Hewlett Packard 5840A gas chromatograph, was accomplished by using a Hewlett Packard automatic sampler (Model 7671A). The analytical column was a 7.5 ft x 1/8 in S.S. tube packed with 15 percent Carbowax 20M on 80/100 mesh Chromosorb W. A temperature program was used, starting at 70° C for 5 minutes and increasing to 125° C at the rate of 4° C per minute. A hold of 8 minutes was used on the final temperature. Helium (30 cc/minute) was used as the carrier gas.

Quantification of pentane, heptane, octane, benzene, toluene, and xylenes was accomplished by preparing four calibration standards for each component. Each standard was individually prepared by injecting a known volume of each component into a known volume of carbon disulfide. The four data points were used to establish a best fit line from the linear regression method. The weight of each component was determined by comparing the peak area of the sample to the calibration line. This weight was corrected for desorption efficiency, and the time-weighted exposure level was calculated in milligrams-per-cubic-meter and converted to ppm. Figure 7 shows a replication of the chromatographic analysis made of the parent, 3M monitor, and charcoal tube samples.

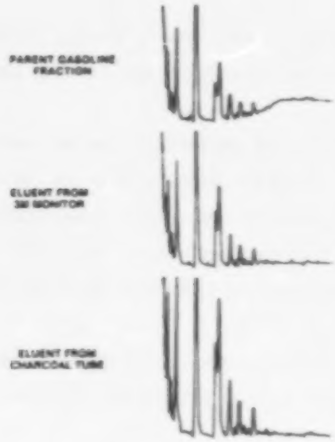


FIGURE 7. Chromatographic analysis gasoline exposure.

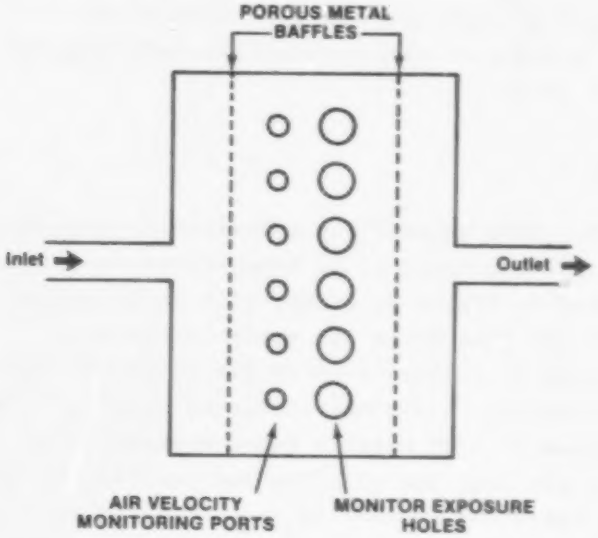

POROUS METAL BAFFLES
Inlet
Outlet
AIR VELOCITY MONITORING PORTS
MONITOR EXPOSURE HOLES

FIGURE 8. Monitor exposure chamber air velocity study.

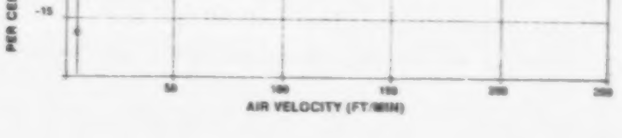


FIGURE 9. Air velocity dependence (parallel-to-face).

The chromatographs are identical except for peak amplitude, which illustrates that both monitoring techniques sample each vapor as if it were present individually.

The desorption efficiencies for components of gasoline were determined in the presence of one another. The recovery tests were done on both the charcoal tubes and the 3M monitors. A known amount of each component was injected onto 100 mg sections of the charcoal tubes or onto a piece of Whatman filter paper 2.5 cm in diameter in the 3M monitor, as described earlier.

The analytical results of the charcoal tubes and 3M monitors agree very well with each other, and with the actual test concentration (Table 2).

In all cases, the 3M monitors gave lower standard deviations and better agreement with the challenge environment. The concentration of the selected components in gasoline was determined by injecting known volumes of the light gasoline fraction into known volumes of carbon disulfide and analyzing in the same manner as the monitor samples.

Integration of Concentration Spikes

To verify the ability of the No. 3500 Organic Vapor Monitor to integrate high peak concentrations, several test exposures of 1, 3-butadiene were made using an exposure system as described in Figure 3, except that an injection septum was placed in series between the flow meter and exposure channel. In each case, charcoal tubes were used to collect samples for comparison and correlation of test data. During sampling, a randomly selected charcoal tube was positioned vertically and upstream of a 3M Organic Vapor Monitor. The 3M monitor was positioned in such a way that the air flow was parallel to the face of the monitor. The charcoal tubes had a sampling rate of 52 cm^3-per-minute. The sampling rate of the 3M monitor is 41.3 cm^3-per-minute for the collection of 1, 3-butadiene.

Three different concentration levels were used to challenge the tubes and 3M monitors, and each level was replicated three times. The first concentration used was a single spike generated by injecting 5 ml of butadiene vapor into the air stream at a flow rate of 9.774 liters-per-minute, thus giving a TWA of 528 parts-per-million as determined by the total air volume (flow meter) and the weight of 1, 3-butadiene injected. The next concentration (1,585 ppm) was generated by three injections of 5 ml each. The last test concentration (3,170 ppm) was produced by three injections of 10 ml each. The spike generations were monitored by a total hydrocarbon analyzer equipped with a flame ionization detector. The signal output from the detector was connected to a millivolt recorder to give a chromatogram of each injection. The sampling probe for the total hydrocarbon analyzer was placed downstream from the charcoal tubes and 3M monitors such that no interferences would be caused during the sampling. It was noticed from the recorder chart that each spike was generated in approximately 6 seconds. This means that the actual peak concentration was in the range of half a percent (5,000 ppm) for 5-ml injections, and 1 percent (10,000 ppm) for 10-ml injections. The results are shown in Table 3.

Clearly, both the 3M monitors and the charcoal tubes with pumps effectively integrated the abrupt concentration changes to give a good estimate of the time-weighted average concentration.

Air Velocity Effects

Diffusion-controlled environmental monitors require a slight air movement across or impinging upon the face of the monitor. Use of Equation 1 assumes that the contaminant concentration at the face of the monitor is representative of the overall environment. In stagnant air, the contaminant is removed from the atmosphere by the monitor. This results in a depleted zone at the face of the monitor and an underestimation of the true contaminant concentration. Previous work (3) studied air velocities above 50 fpm.

Experiments were conducted to determine the air velocity requirements for the 3M No. 3500 Organic Vapor Monitor. The exposure apparatus shown in Figure 3 was employed, but the monitor exposure channel was designed as shown in Figure 8.

The air velocity in the exposure channel was controlled by adjusting air flow rate.

Air velocity was calculated from the flow rate and the exposure channel cross-sectional area. Uniformity of air velocity was also measured using an anemometer probe in the ports indicated. Several exposures to known benzene concentrations were made, and the sampling rate was determined. A total of six monitors was exposed at each air velocity level. Elution and analysis were done following standard procedures outlined previously. Figure 9 is a plot of the results.

The plot shows a significant drop in benzene sampling rate below 10 ft/min face velocity. The ± 2 standard deviation error bars indicate considerable variability at low air velocity. This reflects the difficulty in achieving reproducible, uniform, low velocity in the exposure channel. The mean values do, however, conform well to the published sampling rate for benzene at the higher velocities, and the results are believed to be valid. It should be noted that this experiment tested only parallel-to-face air velocity effects, which is the worst case situation.

As a result of these data, it is believed that the air velocity requirements of the 3M Organic Vapor Monitor are minimal and of no concern for personal monitoring. When used as an area sampler, however, placement of the monitor should be considered so that stagnant air areas are avoided. This situation could potentially exist against walls, in corners, etc.

Temperature and Pressure Effects

Both temperature and pressure affect the diffusion rate of gaseous contaminants in air. This could, in principle, lead to substantial monitoring errors using diffusion-controlled monitors. However, the net effects of temperature and pressure are offset to some degree by corresponding changes in contaminant concentration (4). In the case of atmospheric pressure, the change in diffusion rate and concentration offsets each other exactly, and no correction is required. The effect of temperature on diffusion coefficient and concentration is given by Equations 2 and 3.

$$D = f(T^{3/2}) \qquad [2]$$

$$C = f(\frac{1}{T}) \qquad [3]$$

Therefore,

$$\text{Weight collected} = f(T^{1/2})$$

The net temperature effect can be compensated, if desired, by increasing the experimentally determined concentration in mg/m^3 units by 1.08 percent for every 10° F above 70° F (and reducing by 1.08 percent for every 10° F below 70° F).

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Discussion

PETROVICK: Matt Petrovick, EPA. I think you have a very nice little exposure meter. The size particularly appeals to me from the standpoint of human mobility. I think it is something that is easy and nice to wear, and light.

It is the kind of thing that makes room for physiologic data acquisition systems which may be bulky. And, together, I think they fit nicely. That's one of the prime advantages that I think you have.

The other thought that occurs to me is this: Has there been any planning or any designing in an attempt to try and convert some of the measured exposure levels to an electrical signal--for example, such that you may be able to look at the integrated accumulative effects of these pollutants? In other words, the transfer function from the electro-organic chemistry level to some measurable signal that might be able to be placed into a microcomputer or memory, so that if the level is exceeded, an alarm can be issued so that the person who is exposed might be made aware of it? Is there anything like that on the horizon?

BRAUN: I am an engineer at 3M. Sometimes I can understand what our people in Central Research are doing, and I wouldn't be a bit surprised if they are, but my own work has been mostly in the sampling and the diffusional aspects. It could be done. I think you conveyed some very interesting thoughts.

PETROVICK: I have a very strong feeling that that's the way to go if you want to alarm a person. It is no use to send the device to the lab, and, you know, 4 days later find out he was endangered.

BRAUN: That's a good point.

LOCKER: Larry Locker of Solid State Sensors. I think that's an elegant way, but you look at the compounds like mercury, benzene, trichloroethylene--I think the long-term effects of low levels are what are of concern. I think that the idea here is that you can monitor those for an extremely low cost. And usually 4 days is not so bad to know that someone was exposed to 10 or 20 parts-per-million of benzene. He's not going to die on the spot.

BRAUN: I would like to just comment, too, that we are really building a record of safe operations, and that's a good thing to be doing; it really is.

PETROVICK: But to respond to your comment: What about the person working in a factory who has been there 10 years, and he has an accumulative residual of this chemical, whatever it might be, and one of these days, he crosses his tolerance threshold, and it is that day he might sicken or drop dead?

LOCKER: That's why he should have periodic monitoring, according to the NIOSH regulations.

PETROVICK: That's right. But, wouldn't it be nice for him to have some early warning capability, in terms of something he can hear, saying something like: "Hey, get the heck out of the room"? That's the kind of rationale I had in mind.

JENSEN: Janice Jensen, with the EPA in Washington. What kind of interferences are there with a benzene monitor?

BRAUN: Well, you see--the analysis is by GC or GC mass spectrometry or whatever method you utilize; because the monitor, up to the limits we are talking about, would just collect most organics. We haven't worked with all of them, but, you see, the answer is that the interferences, if there are any, are resolved by the analytical instrument.

DEBBRECHT: Fred Debbrecht, AID. I didn't quite understand the calibration system that you used. Are you counting on that benzene evaporating uniformly?

BRAUN: No, we don't care. When you inject the benzene through the septum, you are going to get a rise and then a gradual drop off. The area under the curve that the monitor integrates is milligrams-per-meter cubed. And we don't care if the curve is level or not.

DEBBRECHT: Is the system reasonably similar to charcoal tubes? I assume you have got some adsorbent there?

BRAUN: Yes.

DEBBRECHT: Certainly the efficiencies that charcoal tubes work at are subject to the concentration of material and amount adsorbed, as opposed to an integrated effect. They are not 100 percent efficient in capturing the pollutant.

BRAUN: As a matter of fact, the concentration profile is quite flat up until you enter the device--we know about where it is within 10 percent, so that we can just operate reasonably. The main concept there is that it is a simple, repeatable way to give a known time-weighted average; that's all I am really saying.

HODGESON: The main question about the calibration system is are you collecting all organic data with your exposure?

BRAUN: No; not at all.

HODGESON: How do you know how much; what's the efficiency?

BRAUN: Well, it is moving past the device, and that's just like the configuration we use in the environment. In fact, about 1 percent is all we collect.

HODGESON: One other question. You didn't say much about the actual construction of the device. Is it diffusing through a membrane?

BRAUN: Yes, and then through a static layer of air.

GOLD: I was curious to know whether you looked at the effect of water vapor and temperature?

BRAUN: Yes; part of that qualification procedure is that we analyze results at both high and low humidities. Usually the effect of water vapor is to decrease the range of utility of the monitor by a little bit. Yes, we do that.

GOLD: How about temperature?

BRAUN: Over the temperature range of normal human existence, this effect is negligible--at least for the compounds we are working on.

BREEN: I am not sure if I understood--do you have any data on parts-per-billion exposures?

BRAUN: No. The data I showed were at the 450 parts-per-billion level corresponding to occupational exposures.

WHITE: Are you limited in terms of the sensitivity of the GC mass spectrometry?

BRAUN: That's correct.

WHITE: If you improved the sampling efficiency, as we were discussing with Ed Palmes, you might be able then to go to the ambient exposure levels.

BRAUN: Yes, and then you can make it bigger, like a big sunflower.

BREEN: Well, isn't it part of the problem at the lower levels that you may get quantitative desorption?

BRAUN: We are not sure whether that occurs. That's why we would like to look into it; absolutely. I would like to work with any interested people at this conference to develop this device for use with daily ambient exposures.

A Combination Sorbent System for Broad Range Organic Sampling in Air

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INTRODUCTION

The use of solid sorbent materials as sampling media is rapidly becoming the method of choice for the collection and preconcentration of organic pollutants in air. Unfortunately, no single sorbent material is available that is universally applicable to the broad range of organic compounds that may be present in environmental and workplace samples. For this reason, additional sorbent materials are needed to supplement the sorbent characteristics of the more commonly used materials (e.g., Tenax-GC and activated charcoals) in applications requiring broad range sampling efficiency.

In light of this need, a program has been initiated to evaluate the sorbent characteristics of some commercially available sorbent materials with the aim of finding a suitable combination of sorbents that is capable of efficiently collecting compounds representing a broad range of volatilities and polarities. The ultimate objective of this EPA-sponsored program (Contract No. 68-02-2774) is to develop a portable, sorbent-based collection system that is capable of sampling a wide variety of carcinogenic vapors in ambient atmospheres.

This paper describes the evaluation and selection of the sorbent materials and suggests a technique for estimating the applicability of sorbent materials for sampling a particular compound based on certain compound properties. The anticipated performance characteristics of the selected combination sorbent system are also discussed.

DISCUSSION

Selection of Candidate Sorbents

Before initiating studies to evaluate and select sorbent materials, a comprehensive review was conducted of available literature on the use of solid sorbent materials for sampling organic vapors. Information was collected on specific sampling applications for over 110 compounds using more than 30 different sorbent materials. This survey indicated three major classes of sorbent materials: 1) porous polymers (e.g., Tenax-GC, Porapaks, Chromosorbs, XADs); 2) carbonaceous materials (e.g., activated carbons and charcoals, graphitized carbon black, Ambersorbs); and 3) others (e.g., molecular sieves, silica gel, liquid-coated solid supports).

Generally, the porous polymers were found to have the most desirable properties for air sampling, including low background and low reactivity, as well as high capacities for many compounds. Unfortunately, the porous polymers were found to have little capacity for the more volatile compounds. On the other hand, the carbonaceous materials were noted to have much better capacities for volatile compounds, but are plagued with reactivity problems and problems associated with hydrophilicity. The other sorbent materials generally had intermediate capacities and various associated sampling problems, and they have not been widely utilized in air sampling applications. Specific candidates were selected from these three groups of sorbent materials.

The goal of this selection was to choose a collection of commercially available materials that, when used in an appropriate combination, showed promise for quantitatively trapping compounds varying widely in volatilities and polarities. To do this, it was necessary to compare the trapping capabilities (capacities) of a sorbent for various compounds with parameters that are indicative of volatility and polarity.

Consistent trends in sorbent capacities were seen when related to compound volatilities, as indicated by either vapor pressure or boiling point, with boiling point being the more convenient parameter. Unfortunately, finding a single polarity parameter that resulted in consistent sorbent capacity trends was not as easy.

After considerable effort, an empirically derived relative polarity ranking of compound functionalities was arrived at based on a weighted combination of polarity parameters, including dipole moment, solubility parameter, hydrogen bonding index, and polarity index. The order of polarity obtained by this scheme was hydrocarbons < halogenated compounds < aldehydes ≈ ethers ≈ esters ≈ ketones < nitro compounds < nitriles ≈ strong acids < amines < alcohols ≈ phosphates < water. This functionality ranking was used in plots of boiling point versus relative polarity for a variety of compounds, and consistent trends were observed for most of the available sorbent capacity data when superimposed on these plots.

On the basis of these plots and related capacity information, Tenax-GC, Porapak N, Porapak R, Ambersorb XE-340, and SKC activated charcoal were selected for further evaluation.

These five sorbents represent three porous polymers and two carbonaceous materials that have a variety of individual properties and the potential, in some combinations, to effectively sample compounds of a wide range of polarities and volatilities. Tenax-GC was selected for the collection of moderately high to high boiling compounds, since it has a high temperature limit. Tenax also has a slight preference for nonhydrogen-bonding compounds. For moderately boiling compounds, the literature showed Porapak R to have the greatest capacity, although retention time data indicated that Porapak N (for which there were no capacity data) might actually have greater capacity. These two Porapaks also show a preference for polar compounds. For highly volatile compounds, a conventional activated charcoal (SKC coconut) was chosen for evaluation, since activated carbons have traditionally been used in such sampling applications. However, a new sorbent material, Ambersorb XE-340 (Rohm and Haas) was also included since it showed promising capacities for highly volatile compounds (e.g., 81 l/g for butane [3]) without some of the undesirable characteristics of charcoals (e.g., hydrophilicity).

Selection of Test Compounds

In order to evaluate the selected sorbent materials for their sampling capabilities, it was necessary to establish a matrix of test compounds that sufficiently describe the ranges of volatilities and polarities that could reasonably be anticipated. Entries were sought for a matrix described by low, medium, and high polarity in one dimension and low, medium, and high volatility in the other. The ranges were established on the basis of relative boiling points for volatility and compound functionality, as previously

TABLE 1

Test Compound Matrix

		Polarity	
	Hydrocarbons and halogenated compounds	Halogenated compounds, aldehydes, ethers, ketones and esters	Nitro compounds, nitriles, amines, and strong acids, alcohols and phosphates
Volatility	Low	Medium	High
Low	n-Hexadecane [1] Phenanthrene [10]	Hexachloro-1,3-butadiene [2] 4-Bromodiphenylether [11]	Succinonitrile [3] *o*-Nitroaniline [12]
Medium	iso-Octane [4] Naphthalene [13]	bis-(2-Chloroethyl) ether [5] 1,2,4-Trichlorobenzene [14]	Ethylene glycol [6] Nitroanisole [15]
High	n-Butane [7] Benzene [16]	Propylene oxide [8] Benzyl chloride [17]	Acrylonitrile [9] Phenol [18]

Note: Bracketed numbers are used to identify these compounds in Figures 5, 8, and 9.

described, for relative polarity. An aliphatic and an aromatic entry were chosen for each point in the matrix. The test compound matrix is shown in Table 1.

Capacity Studies

The evaluation of the sorbent materials (Tenax-GC, Porapak R, Porapak N, Ambersorb XE-340, and SKC activated charcoal) began with studies of the abilities of these sorbents to quantitatively trap various organic compounds. Capacities were determined for as many of the 18 test matrix compounds as possible on each of the five sorbents. Additionally, some low molecular weight aliphatics (methane, ethane, propane, pentane, and hexane) were used to evaluate the carbonaceous sorbents, Ambersorb XE-340 and SKC activated charcoal, for their abilities to trap extremely volatile materials.

The experimental technique that was used to estimate sorbent capacities is a commonly cited, gas chromatographic technique involving the generation of Arrhenius plots. This technique involved packing chromatographic columns (3 ft, 1/4 in O.D., 2 mm I.D.) with known weights of each of the five sorbent materials and conditioning these columns according to the specifications of the sorbent manufacturer. A column was then placed within a gas chromatograph and set at its highest allowable temperature under a flow of 30 ml/min of nitrogen. Samples of the test matrix and/or low molecular weight aliphatic compounds were then injected into the column and detected by a flame ionization

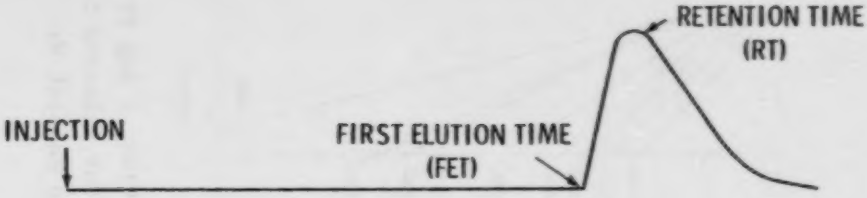


FIGURE 1. Elution analysis method for sorbent capacity determinations.

detector (FID). Sample sizes were within the Henry's Law region such that retention times were not affected by variations. The data obtained included the retention time (RT), which was considered to be the amount of time from injection to peak maximum, and the first elution time (FET), which was the

TABLE 2

Retention Times and Capacities for Selected Test Compounds on Porapak R

Temperature (°C)	Compound				
	n-Butane	Propylene oxide	Acrylonitrile	iso-Octane	Benzene
222	RT = 0.17 min $50\%_{Vg}$ = 8.22 x 10^3 ℓ/g FET = 0.04 min FET_{Vg} = 1.94 x 10^3 ℓ/g	RT = 0.20 min $50\%_{Vg}$ = 9.68 x 10^3 ℓ/g FET = 0.05 min FET_{Vg} = 2.42 x 10^3 ℓ/g	RT = 0.24 min $50\%_{Vg}$ = 11.6 x 10^3 ℓ/g FET = 0.12 min FET_{Vg} = 5.81 x 10^3 ℓ/g	RT = 0.85 min $50\%_{Vg}$ = 41.1 x 10^3 ℓ/g FET = 0.40 min FET_{Vg} = 19.4 x 10^3 ℓ/g	RT = 0.47 min $50\%_{Vg}$ = 22.7 x 10^3 ℓ/g FET = 0.25 min FET_{Vg} = 12.1 x 10^3 ℓ/g
182	RT = 0.26 min $50\%_{Vg}$ = 12.6 x 10^3 ℓ/g FET = 0.10 min FET_{Vg} = 4.84 x 10^3 ℓ/g	RT = 0.33 min $50\%_{Vg}$ = 16.0 x 10^3 ℓ/g FET = 0.15 min FET_{Vg} = 7.26 x 10^3 ℓ/g	RT = 0.46 min $50\%_{Vg}$ = 22.3 x 10^3 ℓ/g FET = 0.35 min FET_{Vg} = 16.9 x 10^3 ℓ/g	RT = 2.67 min $50\%_{Vg}$ = 129 x 10^3 ℓ/g FET = 2.0 min FET_{Vg} = 96.8 x 10^3 ℓ/g	RT = 1.12 min $50\%_{Vg}$ = 54.2 x 10^3 ℓ/g FET = 0.80 min FET_{Vg} = 38.7 x 10^3 ℓ/g
150	RT = 0.50 min $50\%_{Vg}$ = 24.2 x 10^3 ℓ/g FET = 0.30 min FET_{Vg} = 14.5 x 10^3 ℓ/g	RT = 0.68 min $50\%_{Vg}$ = 32.9 x 10^3 ℓ/g FET = 0.40 min FET_{Vg} = 19.4 x 10^3 ℓ/g	RT = 1.00 min $50\%_{Vg}$ = 48.4 x 10^3 ℓ/g FET = 0.8 min FET_{Vg} = 38.7 x 10^3 ℓ/g	RT = 10.33 min $50\%_{Vg}$ = 500 x 10^3 ℓ/g FET = 8.45 min FET_{Vg} = 409 x 10^3 ℓ/g	RT = 3.23 min $50\%_{Vg}$ = 156 x 10^3 ℓ/g FET = 2.60 min FET_{Vg} = 126 x 10^3 ℓ/g
100	RT = 2.11 min $50\%_{Vg}$ = 102 x 10^3 ℓ/g FET = 1.6 min FET_{Vg} = 77.4 x 10^3 ℓ/g	RT = 3.49 min $50\%_{Vg}$ = 169 x 10^3 ℓ/g FET = 2.9 min FET_{Vg} = 140 x 10^3 ℓ/g	RT = 6.35 min $50\%_{Vg}$ = 307 x 10^3 ℓ/g FET = 5.4 min FET_{Vg} = 261 x 10^3 ℓ/g	RT = 150 min $50\%_{Vg}$ = 7,260 x 10^3 ℓ/g FET = 125 min FET_{Vg} = 6,050 x 10^3 ℓ/g	RT = 28.6 min $50\%_{Vg}$ = 1,380 x 10^3 ℓ/g FET = 23.5 min FET_{Vg} = 1,140 x 10^3 ℓ/g

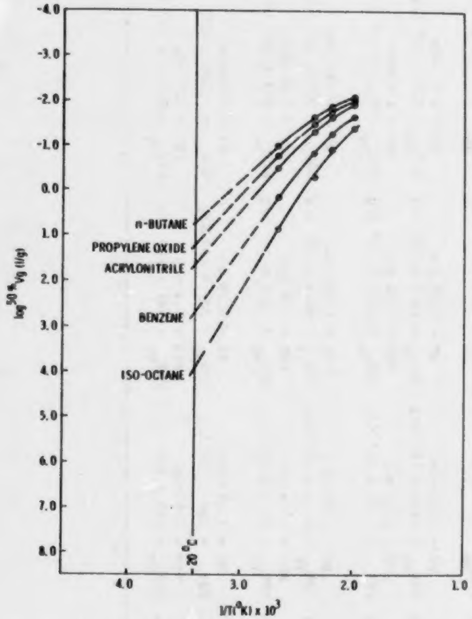


FIGURE 2. Plot of log $50\%_{Vg}$ versus 1/T for selected test compounds on Porapak R.

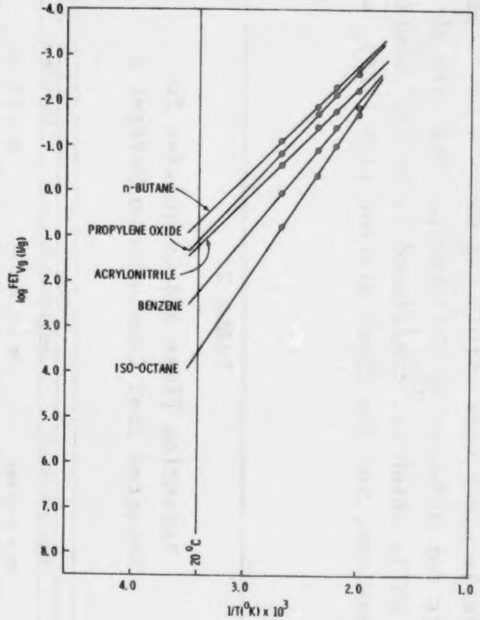


FIGURE 3. Plot of log FET_{Vg} versus 1/T for selected test compounds on Porapak R.

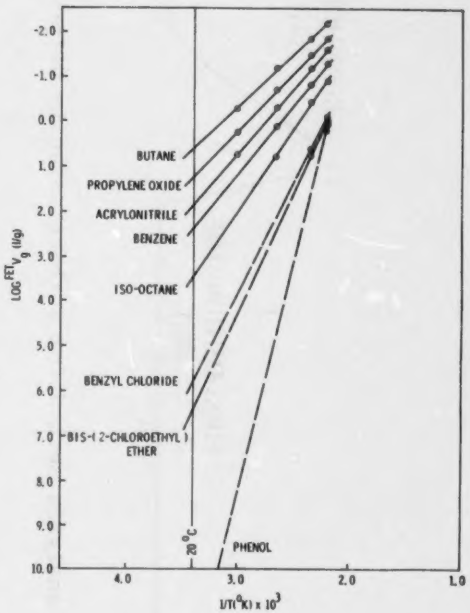


FIGURE 4. Plot of log FET_{Vg} versus 1/T for selected test compounds on Porapak N.

TABLE 3

Volumetric Capacities for Selected
Test Compounds on Porapak R at 20° C

COMPOUND NAME	FET_{Vg} (1/g)
n-Butane	4.93
Propylene oxide	12.4
Acrylonitrile	16.8
iso-Octane	3,550
Benzene	175

time from injection to peak initiation. These points are indicated in Figure 1. By multiplying the retention times and first elution times by the flow rate, and dividing by the amount of sorbent within the chromatographic column, the 50 percent ($50\%_{Vg}$) and FET (FET_{Vg}) volumetric capacities, respectively, were obtained. Sample injections were then made at a variety of column temperatures to obtain similar data.

An example of the experimental information obtained with Porapak R is given in Table 2. These data were used to obtain an Arrhenius plot (log Vg versus 1/T). Figures 2 and 3 are examples of these plots for the $50\%_{Vg}$ and FET_{Vg} values, respectively, for Porapak R. The FET_{Vg} values were then extrapolated to 20° C to obtain the approximate ambient volumetric capacities, $FET_{Vg(20° C)}$, of this sorbent for the test compounds. Table 3 gives this information for Porapak R.

The volumetric capacities, for as many of the test matrix and low molecular weight aliphatic compounds as possible, were determined for the other sorbent materials in a similar manner from the plots shown in Figures 4, 5, 6, and 7. They are compiled in Table 4.

The volumetric capacities (1/g) determined in these evaluations estimate the volume of air that can be sampled per gram of sorbent materials before sample breakthrough (i.e., exceeding capacity). This was determined to be the most applicable measure of capacity for our studies since we wish to sample quantitatively (i.e., no breakthrough).

Methods (2) are available for determining saturation (or weight) capacities, but for this project it was felt that sampling techniques, such as

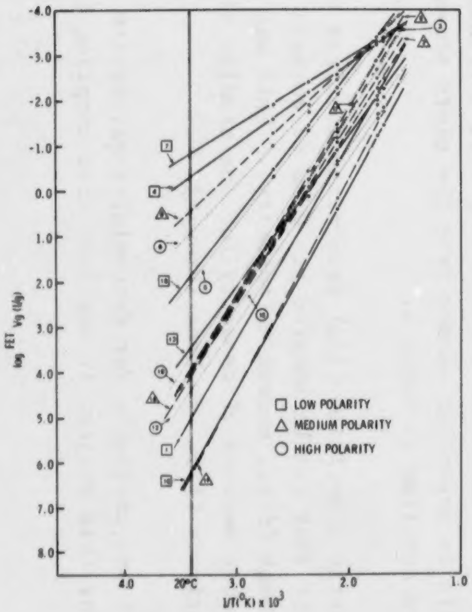


FIGURE 5. Plot of log FET_{Vg} versus 1/T for all test compounds on Tenax-GC. Numbers correspond to bracketed numbers in Table 1.

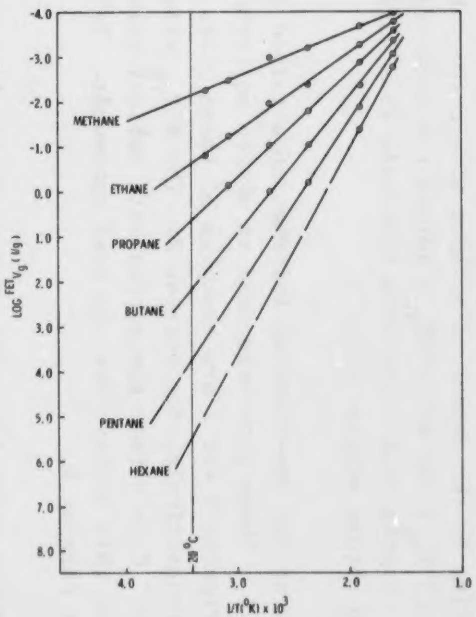


FIGURE 6. Plot of log FET_{Vg} versus 1/T for standard gases on Ambersorb XE-340.

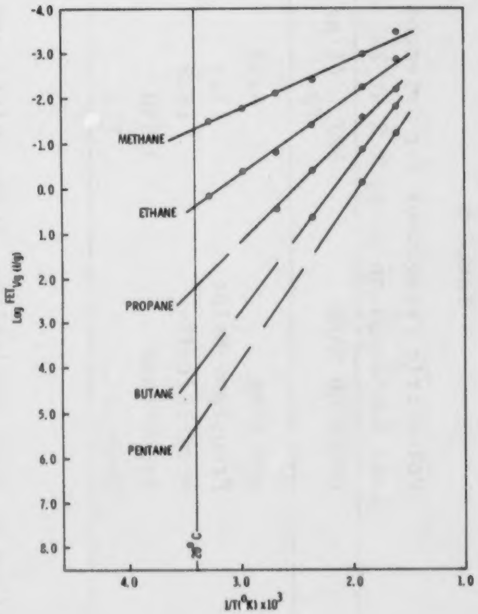


FIGURE 7. Plot of log FET_{Vg} versus 1/T for standard gases on SKC charcoal.

TABLE 4

Compilation of Capacity and Solubility Parameter Data

Key	Name	δ_m (lit)	δ_m (calc)	MW	Tenax-GC		Porapak R		Porapak N		Ambersorb XE-340		SKC charcoal	
					$^{FET}V_g$(20°C) (ℓ/g)	log $^{FET}V_g$	$^{FET}V_g$(20°C) (ℓ/g)	log $^{FET}V_g$	$^{FET}V_g$(20°C) (ℓ/g)	log $^{FET}V_g$	$^{FET}V_g$(20°C) (ℓ/g)	log $^{FET}V_g$	$^{FET}V_g$(20°C) (ℓ/g)	log $^{FET}V_g$
A	Methane	89	-	16.04	-	-	-	-	-	-	0.009	-2.046	0.047	-1.328
B	Ethane	180	-	30.07	-	-	-	-	-	-	0.229	-0.640	2.40	0.380
C	Propane	282	282	44.09	-	-	-	-	-	-	5.33	0.727	162	2.210
D(7)	n-Butane	395	401	58.12	0.16	-0.800	4.93	0.693	3.9	0.591	106	2.025	12 x 10^4	4.079
E	n-Pentane	505	519	72.15	-	-	-	-	-	-	7500	3.875	2 x 10^5	5.301
8	Propylene oxide	534	-	58.08	3.14	0.497	12.4	1.092	17.6	1.246	-	-	-	-
9	Acrylonitrile	557	573	53.06	9.35	0.971	16.8	1.225	69	1.839	-	-	-	-
F	n-Hexane	629	638	86.17	-	-	-	-	-	-	4 x 10^5	5.602	-	-
16	Benzene	719	719	78.11	82	1.914	175	2.244	239	2.378	-	-	-	-
4	iso-Octane	788	834	114.22	0.532	-0.274	3550.	3.550	2900	3.462	-	-	-	-
6	Ethylene glycol	906	-	62.07	120	2.070	-	-	-	-	-	-	-	-
3	Succinonitrile	-	1073	80.09	1.04 x 10^4	4.015	-	-	-	-	-	-	-	-
18	Phenol	1176	-	94.11	5460	3.737	-	-	3 x 10^{12}[b]	12.477[b]	-	-	-	-
17	Benzyl chloride[a]	-	1253	126.58	1.02 x 10^4	4.007	-	-	6.6 x 10^5	5.820	-	-	-	-
13	Naphthalene	1269	1410	128.16	3260	3.513	-	-	-	-	-	-	-	-
5	Bis-(2-chloroethyl) ether[a]	1402	1402	143.02	1.06 x 10^4	4.025	-	-	2.8 x 10^6	6.443	-	-	-	-
12	*o*-Nitroaniline	-	1657	138.12	2.9 x 10^4	4.460	-	-	-	-	-	-	-	-
15	*m*-Nitroanisole	-	1684	153.13	1.14 x 10^4	4.058	-	-	-	-	-	-	-	-
10	Phenanthrene	1747	-	178.22	1.9 x 10^6	6.282	-	-	-	-	-	-	-	-
1	n-Hexadecane	1811	1766	226.43	1.3 x 10^5	5.113	-	-	-	-	-	-	-	-
14	1,2,4-Trichlorobenzene[a]	-	2014	181.46	1.57 x 10^4	4.195	-	-	-	-	-	-	-	-
11	4-Bromodiphenyl ether[a]	-	2616	249.11	2.4 x 10^6	6.377	-	-	-	-	-	-	-	-
2	Hexachloro-1,3-butadiene[a]	-	2783	267.6	1.15 x 10^4	4.059	-	-	-	-	-	-	-	-

[a] Halogenated.

[b] Potentially large experimental error.

the use of backup tubes and varying sampling volumes, would be an appropriate manner of obtaining valid samples in the event of highly concentrated samples.

As it is a long and arduous task to determine the capacities of a large number of compounds on several sorbent materials by the method just described, it was thought that a means of correlating sorbent capacities with compound properties would be highly desirable. Such a means of correlation would permit the estimation of the $\text{FET}_{Vg(20° C)}$ of any compound on any sorbent by knowing the value of the particular property or properties, and how this property is related to sorbent capacity. Then, if a change or addition should occur in the list of compounds of interest, one could state whether the new compound is probably, possibly, or not likely to be quantitatively trapped by a particular sorbent under certain conditions. If sorbent materials were used in series for sample collection, one would also have an idea of on which sorbent the majority of a certain compound is likely to appear. The general advantage of a means of correlating sorbent capacity and compound properties would be to eliminate the necessity of experimentally determining the capacity of every compound on every sorbent.

The forces that determine the interaction of an organic compound with other materials (neglecting vapor-to-liquid phenomena of nucleation and growth) are: E_d, the dispersion or London forces; E_p, the permanent dipole/dipole forces; and E_h, the hydrogen-bonding forces. These forces are additive, and the total interaction energy may be expressed as $E = E_d + E_p + E_h$. Dividing both sides by the nuclear volume of the material, one obtains:

$$E/V = \frac{E_d + E_p + E_h}{V}$$

Since $$\delta + \left(\frac{E}{V}\right)^{1/2} = \text{cohesive energy density}$$

where δ is the solubility parameter, then

$$\delta = \delta_d^2 + \delta_p^2 + \delta_h^2$$

The solubility parameter has been well described in the literature (1). Many experimental methods exist to determine δ for a compound, and many more methods exist for estimating δ from compound properties such as surface tension. A very useful method of estimating δ from the structural formula, density, and molecular weight of a compound has been developed by Small (4).

Accordingly, δ_d, δ_p, δ_h, and δ were examined for a number of compounds. No correlation of the separate or total forces with the $FET_{Vg(20° C)}$ was found. One would expect a correlation with the dominant force factor, if one should exist, and a correlation with δ would seem even more reasonable. However, of two compounds with similar δ values, the compound with the higher molecular weight (or size) would be expected to have a larger $FET_{Vg(20° C)}$ on a given sorbent due to its lesser volatility. Therefore, various molecular weight adjustments of δ were tried. The simple expedient of multiplying δ by the molecular weight gives a relative size dependent factor, $\delta_m = \delta \times MW$, which has the units of $(g^2 \times cal)^{1/2}/(cm^3 \times mole)$. The molecular weight modified solubility parameters (δ_m) for the test matrix and low molecular weight aliphatic compounds, both from literature and calculated (2) solubility parameter values, are given in Table 4 along with sorbent capacity data. The data for δ_m are plotted versus the log $FET_{Vg(20° C)}$ for SKC charcoal, Ambersorb XE-340, Porapak N, and Tenax-GC in Figure 8, and for Porapaks R and N in Figure 9. The correlation coefficients for the "best" lines in these figures are given in Table 5.

Note that the most divergent results occur for a few halogenated compounds on Tenax-GC. Unusual behavior of such compounds on Tenax-GC had been noted previously during capacity studies. It was postulated that some sort of solubility effect was possible occurring, since Tenax-GC has a solubility parameter similar to that of halogenated compounds and is known to be soluble in such halogenated solvents as chloroform, carbon tetrachloride, and methylene chloride.

Desorption Properties

A number of experiments were conducted to determine how amenable the candidate sorbents are to thermal desorption. These experiments were of a preliminary nature, since desorption properties are compound dependent, and the test matrix compounds are not necessarily the compounds that will be of interest in future field studies. The preliminary experiments that were conducted attempted to evaluate the sorbents for efficient compound desorption and extraneous background due to contamination and/or sorbent characteristics.

For the desorption efficiency experiments, 6-in long, 1/4 in O.D., 4 mm I.D. glass sampling tubes were packed with the sorbent materials listed in Table 6 and evaluated on the desorption/analytical system depicted in Figure 10. Note that the Chromalytics Concentrator® oven contains a six-port, two-position valve which is sketched in Figure 11. This valve offers the alter-

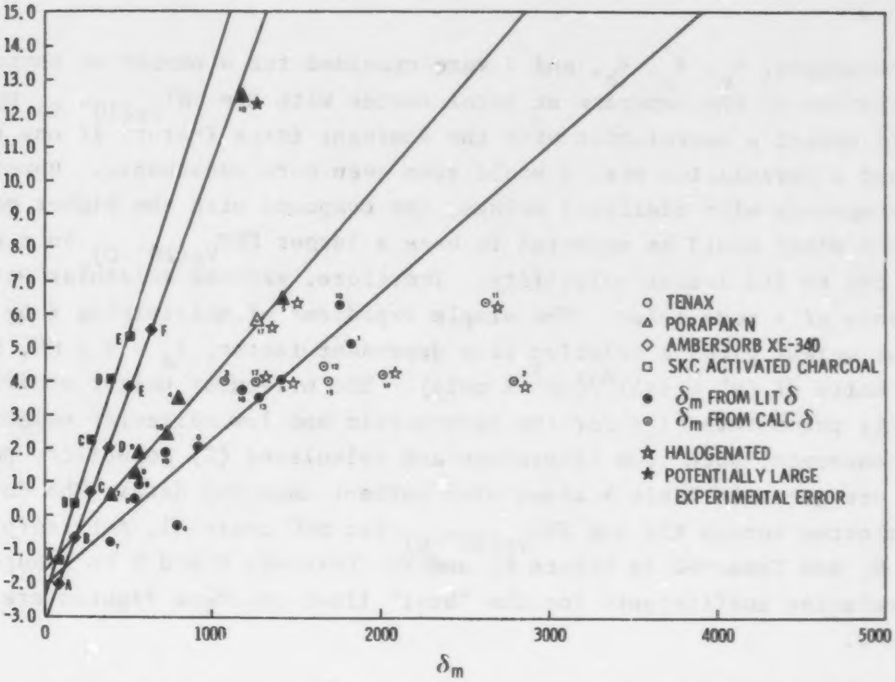


FIGURE 8. Correlation of δ_m and log FET$_{Vg(20° C)}$ for test compounds on sorbent materials. Entries correspond to key in Table 4.

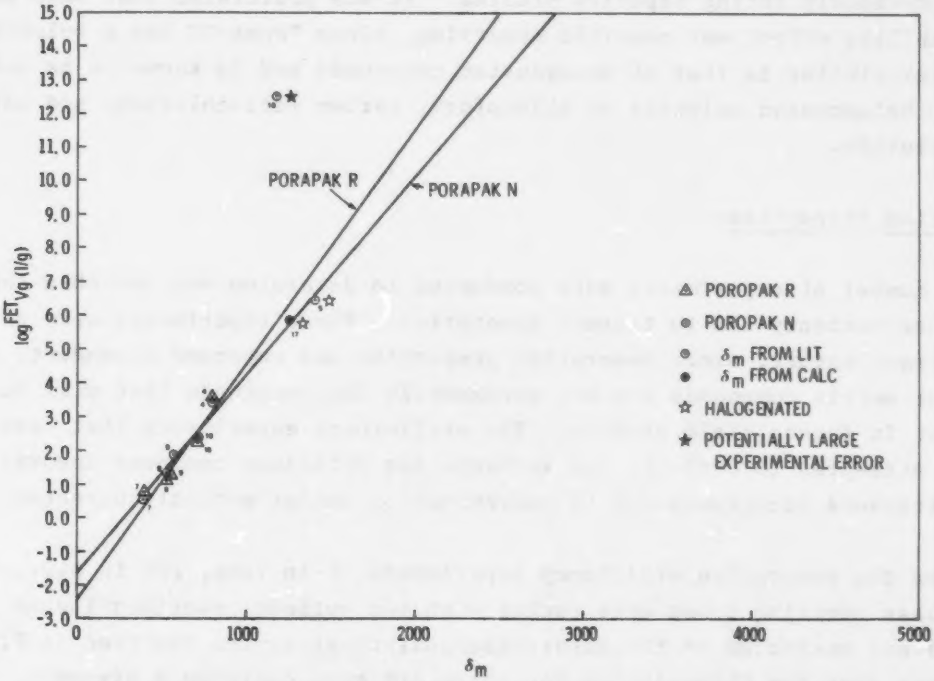


FIGURE 9. Correlation of δ_m and log FET$_{Vg(20° C)}$ for selected test compounds on Porapaks R and N. Entries correspond to key in Table 4.

TABLE 5

Correlation Coefficients for the "Best" Lines of δ_m versus Log $FET_{Vg(20° C)}$ Plots (Figures 8 and 9)

SORBENT MATERIAL	$FET_{Vg(20° C)}$ CORRELATION COEFFICIENT
SKC charcoal	0.996
Ambersorb XE-340	0.999
Porapak N	0.993
Porapak R	0.944
Tenax-GC	0.806
Tenax-GC (excluding halogenated compounds)	0.916

native of direct syringe injection of a standard or thermal desorption of a sampling tube. Standards were prepared with a 1,000 μg/ml concentration in acetone and stored in septum-capped vials. Chromatographic conditions were established by direct injections of standards using a 7 ft, 1/4 in O.D., 2 mm I.D. glass analytical column containing 1.125 g of Tenax, which was conditioned at 320° C overnight. For statistical determination, replicate, direct injections (∿1 μl) were made of each standard under the chosen chromatographic conditions and the areas of the peaks integrated by a Hewlett-Packard Model 3354 Lab Automation System. Sampling tubes were placed in the desorption chamber, conditioned briefly (∿30 min), and quickly investigated for background under the desorption/chromatographic conditions to be used. Injections (∿1 μl) of the prepared standards were made onto the far ends (i.e., furthest from the analytical column) of the sampling tubes, with subsequent thermal desorption into the analytical column for chromatography and peak integration. Desorption efficiencies were determined in the following manner:

$$\text{Desorption efficiency} = \frac{\text{(Area of peak from sampling tube desorption)}}{\text{(Average areas/}\mu\text{l of peaks from standard injections)}} \times \frac{100}{\text{[Amount (}\mu\text{l) injected onto sampling tube]}}$$

In order to establish a median and a range, the desorption efficiency was determined at least three times for each compound on each sorbent.

TABLE 6

Sampling Tube Data (All Sorbent Filled Tubes Have Glass Wool Plugs)

Sorbent material	Tube No.	Soxhlet extraction information	Amount of sorbent material (g)	Manufacturer's temperature limit (°C)	Conditioning temperature (°C)	Desorption temperature (°C)
Tenax (60/80 mesh)	38	None	0.1218	400	325	300
Tenax (60/80 mesh)	7	Overnight with MeOH	0.1507	400	325	300
Tenax (60/80 mesh)	33	Overnight with each MeOH, EtOAc and pentane	0.1399	400	325	300
Porapak R (50/80 mesh)	26	None	0.2604	250	175 and 240	170
Porapak R (50/80 mesh)	15	Overnight with MeOH	0.2805	250	175 and 240	170
Porapak N (50/80 mesh)	40	None	0.3735	190	175	170
Porapak N (50/80 mesh)	30	Overnight with MeOH	0.3386	190	175	170
SKC activated charcoal	34	None	0.4165	-	325	300
SKC activated charcoal	27	None	0.5176	-	320	300
SKC activated charcoal	17	None	0.5507	-	320	300
Ambersorb XE-340	41	None	0.6114	-	320	300
Ambersorb XE-340	43	None	0.5234	-	320	300
Ambersorb XE-340	839	None	0.7179	-	325	300
Ambersorb XE-340	847	Overnight with each MeOH and distilled H_2O	0.7201	-	325	300

TABLE 7

Chromatographic Conditions and Raw Data for the Determination of Desorption Efficiencies

Compound	Chromatographic conditions	Average RT of standards	Average area count/µl for standard	Sampling tube	Cond. temp. (°C)	Des. temp. (°C)	Trial	µl Std.	RT	Area counts	Desorption efficiency (%)
iso-Octane	Temperature Programmed from 50°C @ 2°C/min for 10 min then @ 32°C/min to a final 250°C temperature and held there for eight minutes	2.98	15694	Tenax #7	300	300	1	1.10	3.59	16805	97%
							2	1.15	3.35	20929	116%
							3	1.10	2.93	17984	104%
		3.14	(He carrier) 9376	Porapak R #26	235	150	1	1.05	3.95	11075	112%
							2	1.15	3.73	11288	105%
							3	1.09	4.05	10805	106%
		3.32	14713	Porapak N #30	175	150	1	1.15	3.74	19062	113%
							2	1.15	4.07	18906	112%
							3	1.13	4.07	18759	113%
Naphthalene	Temperature Programmed from 150°C to 250°C @ 8°C/min and held at the final temperature for 4 minutes	10.85	346086	Tenax #7	300	300	1	1.10	10.88	368397	97%
							2	1.10	10.89	355569	93%
							3	1.00	10.89	334466	97%
							4	1.00	10.88	327426	95%
		11.33	350729	Porapak R[a] #15	235	220	1	1.19	>30 min	- -	?
		11.30	341814	Porapak N[a] #30	175	150	1	1.16	>30 min	- -	?
Phenanthrene	Temp. Prog. from 200°C to 300°C @ 32°C/min and held 4 minutes	7.72	205658	Tenax #7	300	300	1	0.80	7.85	182183	111%
							2	0.65	8.01	139996	105%
							3	0.80	7.96	181463	110%
n-Hexadecane	Temperature Programmed from 200°C to 250°C @ 4°C/min and held @ 250°C for 4 minutes	9.00	291098	Tenax #7	300	300	1	1.00	9.25	270396	95%
							2	1.10	9.21	312449	98%
		8.95	292206				3	1.15	9.11	333690	99%
							4	1.10	9.10	323293	100%

[a] No indication of a sample desorption under experimental conditions.

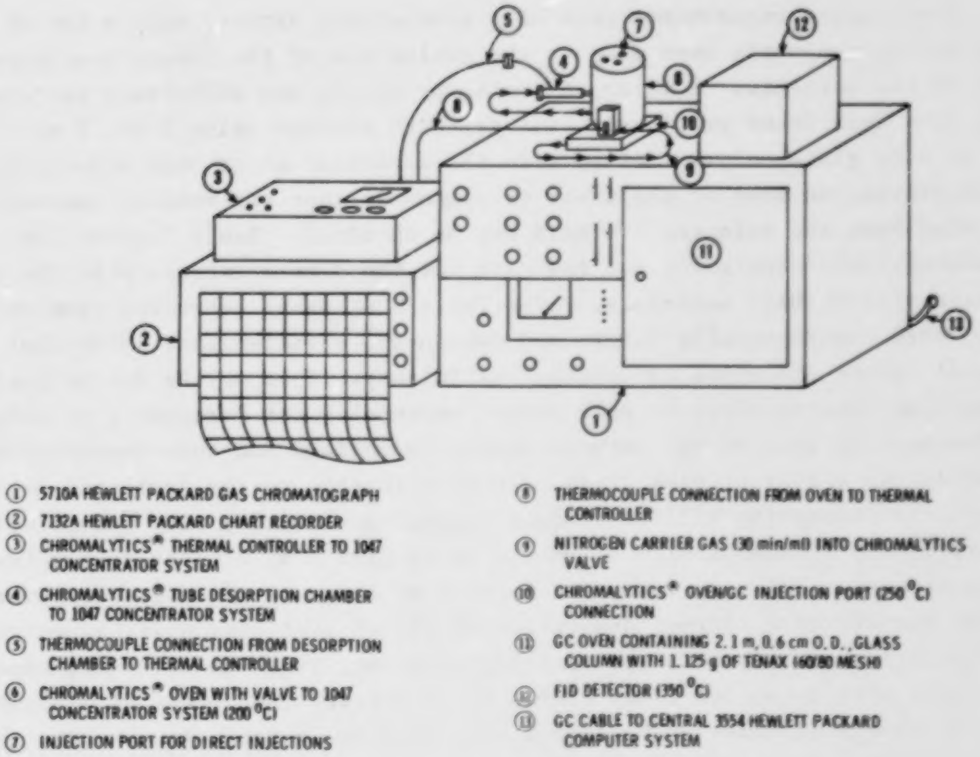

① 5710A HEWLETT PACKARD GAS CHROMATOGRAPH
② 7132A HEWLETT PACKARD CHART RECORDER
③ CHROMALYTICS® THERMAL CONTROLLER TO 1047 CONCENTRATOR SYSTEM
④ CHROMALYTICS® TUBE DESORPTION CHAMBER TO 1047 CONCENTRATOR SYSTEM
⑤ THERMOCOUPLE CONNECTION FROM DESORPTION CHAMBER TO THERMAL CONTROLLER
⑥ CHROMALYTICS® OVEN WITH VALVE TO 1047 CONCENTRATOR SYSTEM (200 °C)
⑦ INJECTION PORT FOR DIRECT INJECTIONS
⑧ THERMOCOUPLE CONNECTION FROM OVEN TO THERMAL CONTROLLER
⑨ NITROGEN CARRIER GAS (30 min/ml) INTO CHROMALYTICS VALVE
⑩ CHROMALYTICS® OVEN/GC INJECTION PORT (250 °C) CONNECTION
⑪ GC OVEN CONTAINING 2.1 m, 0.6 cm O.D., GLASS COLUMN WITH 1.125 g OF TENAX (60/80 MESH)
⑫ FID DETECTOR (350 °C)
⑬ GC CABLE TO CENTRAL 3354 HEWLETT PACKARD COMPUTER SYSTEM

FIGURE 10. Desorption/analytical system used in desorption efficiency evaluations.

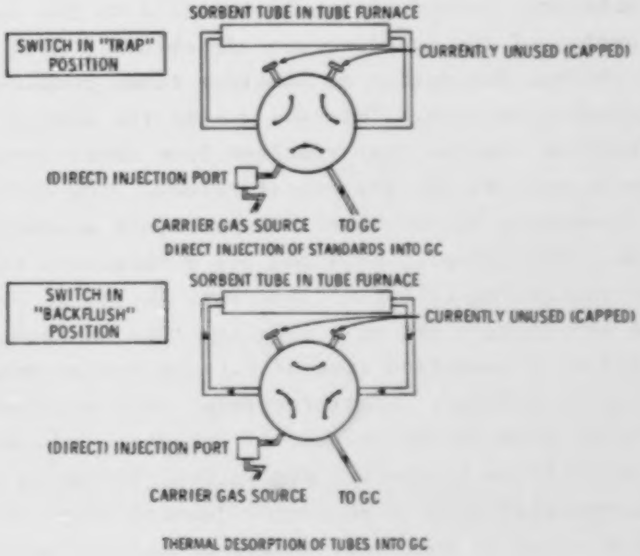

SORBENT TUBE IN TUBE FURNACE
SWITCH IN "TRAP" POSITION
CURRENTLY UNUSED (CAPPED)
(DIRECT) INJECTION PORT
CARRIER GAS SOURCE
TO GC
DIRECT INJECTION OF STANDARDS INTO GC
SORBENT TUBE IN TUBE FURNACE
SWITCH IN "BACKFLUSH" POSITION
CURRENTLY UNUSED (CAPPED)
(DIRECT) INJECTION PORT
CARRIER GAS SOURCE
TO GC
THERMAL DESORPTION OF TUBES INTO GC

FIGURE 11. Diagram of six-port, two-position valve within Chromalytics® oven.

Since these experiments were of a preliminary nature, only a few of the test matrix compounds were used in the evaluation of the desorption properties of the sorbents. However, by relating desorption efficiency to retention time data found previously (for capacity studies using 3 ft, 2 mm I.D., 1/4 in O.D. glass columns filled with the sorbents) at or near desorption temperatures, an idea of the types of compounds that are readily thermally desorbed from the selected sorbents may be obtained. Table 7 gives the chromatographic conditions and raw data for the determinations with the porous polymer type sorbent materials, while Table 8 presents retention time data along with experimentally determined desorption efficiencies. Note that several values are above 100 percent efficiency. This may be due to either background contributions to peak areas (especially for Porapaks), or slight differences in peak shapes between direct injections and tube desorptions resulting in different peak areas. In relationship to the indicated retention times, the desorption efficiency data suggest potentially easy quantitative desorption of compounds with retention times (Table 8) of less than a few (~12) minutes. This, in turn, indicates that Tenax is probably very amenable to the quantitative thermal desorption of all 18 test compounds (assuming no decomposition problems) and potentially of other, less volatile substances. Compounds with retention times (Table 8) of greater than about 12 minutes, such as benzyl chloride on Porapak N, may also be amenable to quantitative thermal desorption if the desorption period is prolonged and the sample reconcentrated in a capillary trap or on the head of the analytical column.

Unfortunately, this experimental procedure, which worked quite adequately for the porous polymers, proved not to be amenable to the evaluation of desorption efficiencies of the carbonaceous adsorbents. Much broader peaks resulted from the thermal desorption of sampling tubes compared with those peaks produced by standard injection. This was due to the longer retention times for thermally desorbed samples that resulted from their having to pass through the sorbent tube as well as the analytical column. The difference in the peak shapes made it impossible to accurately compare peak areas with the standards by this technique. For example, n-butane has a retention time of 0.6 min on a 3-ft column containing 1.11 g of Ambersorb XE-340 at 300° C, but desorption at the same temperature off of a sampling tube containing ~0.6 g of this adsorbent resulted in a retention time of 1.4 min and an average desorption efficiency of only 76 percent. Similar results were obtained for n-butane with charcoal-filled sampling tubes. It is uncertain how amenable these carbonaceous sorbents will be to thermal desorption, but it is possible that with the sample reconcentrated after a prolonged desorption period, some of the more volatile compounds could be analyzed. However, solvent desorption of these

TABLE 8

Retention Time Data and Desorption Efficiencies at or near Desorption Temperature for Sorbent Materials

		Retention time (min)			
		Porapak N	Porapak R		Tenax
Test compound	δ_m	@ 150°C	@ 150°C	@ 222°C	@ 302°C
n-Butane	395	0.51	0.50	0.17	0.10
Propylene oxide	594	1.03	0.68	0.20	0.11
Acrylonitrile	557	1.93	1.00	0.24	0.08
Benzene	719	4.48	3.23	0.47	0.12
iso-Octane	788	12.1 (113±1%)[a]	10.33 (108±4%)	0.85 (>132%)[b]	0.11 (106±10%)
Ethylene glycol	906	-	-	-	0.11
Succinonitrile	1073	-	-	-	0.17
Phenol	1176	-	-	-	0.17
Benzyl chloride	1253	110	-	-	0.16
Naphthalene	1269	- (?)[c]	-	- (?)[c]	0.22 (95±2%)
bis-(2-Chloroethyl)ether	1402	165	-	-	0.15
Nitroaniline	1657	-	-	-	0.41
Nitroanisole	1684	-	-	-	0.33
Phenanthrene	1747	-	-	-	1.02 (109±4%)
n-Hexadecane	1811	-	-	-	0.21 (98±3%)
1,2,4-Trichlorobenzene	2014	-	-	-	0.20
4-Bromodiphenyl ether	2616	-	-	-	0.61
Hexachloro-1,2-butadiene	2783	-	-	-	0.18

[a] Numbers in parentheses are desorption efficiencies.

[b] Significant contribution from sorbent background.

[c] No indication of sample desorption after 30 min at experimental conditions.

TABLE 9

Qualitative Evaluation of Two Sorbent Properties Compared to δ_m to Determine Ranges of Sorbent Utility

Key	Name	δ_m (lit)	δ_m (calc)	Tenax-GC		Porapak R		Porapak N		Ambersorb		SKC Charcoal	
				Trap	Desorb	Trap	Desorb	Trap	Desorb	Trap	Desorb	Trap	Desorb
A	Methane	89	-	00	!	00	!	00	!	00	!	00	!
B	Ethane	180	-	00	!	00	!	00	!	00	!	00	!
C	Propane	282	282	00	!	00	!	00	!	00	!	00	!
D(7)	n-Butane	395	401	00	!	00	!	00	!	00	!	✓	!?
E	n-Pentane	505	519	00	!	00	!	00	!	✓	!?	✓	!?
8	Propylene Oxide	534	-	00	!	00	!	00	!	✓	!?	✓	!?
9	Acrylonitrile	557	573	00	!	00	!	00	!	✓	!?	✓	!?
F	n-Hexane	629	638	00	!	00	!	00	!	✓	!?	✓	X
16	Benzene	719	719	00	!	00	!	00	!	✓	!?	✓	X
4	iso-Octane	788	834	00	!	✓	!	✓	!	✓	X	✓	X
6	Ethylene Glycol	906	-	00	!	✓	!	✓	!	✓	X	✓	X
3	Succinonitrile	-	1073	✓	!	✓	!	✓	!	✓	X	✓	X
18	Phenol	1176	-	✓	!	✓	!?	✓	!?	✓	X	✓	X
17	Benzyl Chloride	-	1253	✓	!	✓	!?	✓	!?	✓	X	✓	X
13	Naphthalene	1269	1410	✓	!	✓	!?	✓	!?	✓	X	✓	X
5	Bis-(2-chloroethyl) Ether	1402	1402	✓	!	✓	!?	✓	!?	✓	X	✓	X
12	o-Nitroaniline	-	1657	✓	!	✓	X	✓	X	✓	X	✓	X
15	m-Nitroanisole	-	1684	✓	!	✓	X	✓	X	✓	X	✓	X
10	Phenanthrene	1747	-	✓	!	✓	X	✓	X	✓	X	✓	X
1	n-Hexadecane	1811	1766	✓	!	✓	X	✓	X	✓	X	✓	X
14	1,2,4-Trichlorobenzene	-	2014	✓	!	✓	X	✓	X	✓	X	✓	X
11	4-Bromodiphenyl Ether	-	2616	✓	!	✓	X	✓	X	✓	X	✓	X
2	Hexachloro-1,3-butadiene	-	2783	✓	!	✓	X	✓	X	✓	X	✓	X

Key to Table

	Probably	Possibly	Not Likely
Trap Quantitatively	✓	✓?	00 (Vg<480 1/g)
Desorb Quantitatively	!	!?	X

TABLE 10

Ranges of Utility of Solid Sorbents Based on δ_m

SORBENT	δ_m (Trap)	To	δ_m (Desorb)
SKC charcoal	~350	to	~600
Ambersorb	~450	to	~750
Porapak N	~750	to	~1,500
Porapak R	~750	to	~1,500
Tenax-GC	~950	to	>2,800

materials may prove to be more desirable.

In addition to desorption efficiencies and retention time data at or near desorption temperature, Table 8 also gives δ_m values for the compounds listed. This table indicates a relationship between these retention times and δ_m, especially for Porapaks R and N. This relationship suggests that δ_m may be used to determine which compounds will be quantitatively desorbed from sorbent materials.

Since a fair correlation has been demonstrated for δ_m and sorbent capacity, and a relationship potentially exists for δ_m and desorption efficiency, then δ_m may be useful in determining which compounds are likely to be quantitatively adsorbed on and subsequently desorbed from a particular sorbent material. A qualitative comparison of δ_m with sorbent capacity and desorption efficiency is given in Table 9. The entries in this table are defined in the key beneath it and are based upon a combination of experimental data, demonstrated correlations, and chemical intuition. The enclosed regions indicate compounds which are probably or possibly quantitatively trapped at a high-volume condition (480 l, corresponding to 1 l/min for 8 hr) and are probably or possibly quantitatively desorbed from the sorbent materials indicated. These regions correspond to ranges of δ_m values which are listed in Table 10.

Based on these results, a sorbent material may be used to sample most compounds with δ_m values falling within its δ_m range. Alternatively, a sorbent material may be selected for sampling studies with a particular compound which has a δ_m value within the δ_m range of utility of the sorbent. For example, a compound with a δ_m value of 2,000 should probably be sampled using Tenax-GC. A compound with a δ_m value of 1,400 falls within the ranges of utility of Porapak N, Porapak R, and Tenax-GC. Since 1,400 is close to the 1,500 δ_m desorption limit of the Porapaks, Tenax-GC would again be the best sorbent (of these five) to evaluate first for sampling this compound. However, a compound with a δ_m value of 1,000 would probably be easier to sample using one of the Porapaks, since this value is near the δ_m trapping limit of Tenax-GC. A problem potentially exists for compounds with δ_m values around 750, since this is the δ_m desorption limit of Ambersorb XE-340 and the δ_m trapping limit of Porapaks R and N. Therefore, for a complex organic sample, some overlap exists for the ranges of utility (and the types of compound sampled) of Tenax-GC and the Porapaks, but a potential gap exists between the ranges of utility of these polymeric adsorbents and the carbonaceous adsorbents. It should be emphasized that these ranges are only estimates of sorbent utility, and it is likely that some compounds may not adhere to this scheme.

The other area of interest during the evaluation of the thermal desorption properties of the selected sorbent materials was potential extraneous background resulting from contamination and/or sorbent characteristics. Sorbent backgrounds can be composed of a variety of contaminants from a number of different sources. Depending upon the degree and nature of these contaminants, they can lead to complications during both sample collection and analysis. In order to minimize problems from background contamination, it is best to know as much as possible about what types of contamination can arise, how they usually occur, and how best to minimize all sources of contamination. In this way, complications--such as in situ reactions and interference during analysis--can be minimized and possibly avoided.

Generally, all commercial sorbent materials as received from suppliers contain significant levels of background contamination as the result of production, packaging, and/or transportation. Although most of this initial contamination may be removed by solvent (before packing in tubes) and/or thermal (usually after packing in tubes) conditioning, such conditioning may also introduce contaminants. Backgrounds may be introduced from trace impurities in the solvent and the gas stream, and also from decomposition products of the polymer. Obviously one does not heat a polymer above its temperature limit or extract it in a solubilizing solvent, but some polymeric breakdown can occur under other situations as well. Each sorbent will have thermal properties that are unique, and, therefore, conditioning procedures should be validated and optimized for each sorbent material. As a precaution, one should also be aware of the types of compounds each sorbent produces as the result of thermal and/or chemical degradation. Table 11 lists several of the major thermal decomposition products that could be expected from the selected sorbent materials, as well as the chemical compositions and tempera-

TABLE 11

Expected Thermal Decomposition Behavior of Selected Sorbent Materials

Sorbent	Chemical composition	Temperature limit (°C)	Major thermal decomposition products
Porapak N	N-vinyl pyrrolidone	190	Vinyl pyrrolidone Pyrrolidone Pyrrilidiene
Porapak R	N-vinyl pyrrolidone	250	Vinyl pyrrolidone Pyrrolidone Pyrrilidiene
Tenax-GC	2,6-Diphenyl-*p*-phenylene oxide	400	Alkyl benzenes Styrene Benzene Alkyl phenols
Ambersorb XE-340	Carbonized styrene-divinyl benzene	>350	?
SKC activated charcoal	Carbonized organics	>400	?

ture limits of the sorbents. Since the temperature limit of Ambersorb XE-340 was not stated by its manufacturer, a freshly packed 3 ft, 1/4 in O.D., 2 mm I.D. glass column of this sorbent was prepared, conditioned, and analyzed by GC/MS to verify that thermal decomposition was not occurring at the conditioning temperature of 350° C. This column was placed in the GC oven of a Hewlett-Packard Model 5982A GC/MS system and subjected to stepwise temperature increases (50° C intervals) up to 250° C. The effluent from the column was continuously monitored by mass spectrometry and showed none of the expected thermal decomposition products of the styrene-divinyl benzene polymer. Indeed, the only effluents observed were CO_2, SO_2, argon, and traces of a few low molecular weight aliphatics. Therefore, thermal decomposition of Ambersorb XE-340 does not occur at 350° C, which is above the anticipated operating temperatures.

Once the conditioning procedure for a particular sorbent has been established, care must be taken to prevent additional contamination during subsequent handling. The handling and storing of sampling tubes should be optimized without being unreasonably complicated or expensive. The techniques developed should also ensure the integrity of all samples collected (i.e., no sample loss).

Finally, backgrounds from other sources in the desorption/analytical system should be eliminated or reduced to the greatest extent possible. These can arise not only from the usual sources of chromatographic background contamination (e.g., column and septum bleed), but also from sources that are unique to the method of desorption and sample introduction. These less obvious difficulties could include dust being introduced into the desorption chamber, or fingerprints on the sample tube, depending upon the desorption chamber design. Generally, background contamination introduced by a desorption/analytical system are best minimized by using forethought when designing the system.

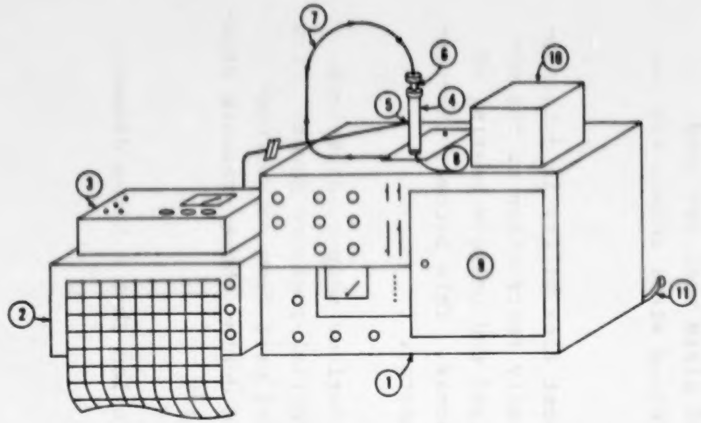
A series of experiments was conducted to evaluate the background levels of the materials being studied and possible sources of background within the desorption/analytical system. Sampling tube backgrounds were evaluated by using the desorption/analytical system sketched in Figure 12 and the sampling tubes listed previously in Table 6. The following are some of the findings determined during these evaluations of sorbent backgrounds.

Conditioning.

- No difference was noted between solvent extracted and nonsolvent extracted sorbents (for the sorbents studied and the experimental system used).
- For Porapak R, conditioning at 240° C produced less background upon desorbing at 170° C than with conditioning at 175° C and desorbing at 170° C.
- Thermal conditioning removed a great deal of contamination, most within the first hour.
- After conditioning, the backgrounds of Porapak R and N tubes were above the background of a blank (empty) control tube, while the backgrounds of Tenax-GC, Ambersorb XE-340, and SKC activated charcoal matched the background level of the blank control tube.

Handling and Storage.

- A desorption system designed to eliminate the exterior of the sampling tube from analytical desorption greatly diminishes problems with handling and storage.
- Capping tubes with metal fittings and storing them in culture tubes with Teflon-lined caps seems to be the best method of tube storage to eliminate extraneous contamination.
- Glass sampling tubes offer a more inert surface than stainless steel,



① 5710A HEWLETT PACKARD GAS CHROMATOGRAPH
② 7132A HEWLETT PACKARD CHART RECORDER
③ CHROMALYTICS THERMAL CONTROLLER TO 1047 CONCENTRATOR SYSTEM
④ CHROMALYTICS TUBE DESORPTION CHAMBER TO 1047 CONCENTRATOR SYSTEM
⑤ THERMOCOUPLE CONNECTION FROM DESORPTION CHAMBER TO THERMAL CONTROLLER
⑥ DESORPTION CHAMBER ENTRANCE AND (O-RING) SEAL
⑦ NITROGEN CARRIER GAS (30 ml/min)
⑧ DESORPTION CHAMBER/GC INJECTION PORT (300 °C) CONNECTION
⑨ GC OVEN (320 °C) CONTAINING EMPTY 0.9 m, 0.6 cm O.D., 2 mm I.D. GLASS COLUMN
⑩ FID DETECTOR (350 °C)
⑪ GC CABLE TO CENTRAL 3554 HEWLETT PACKARD COMPUTER SYSTEM

FIGURE 12. Desorption/analytical system used in tube background evaluations.

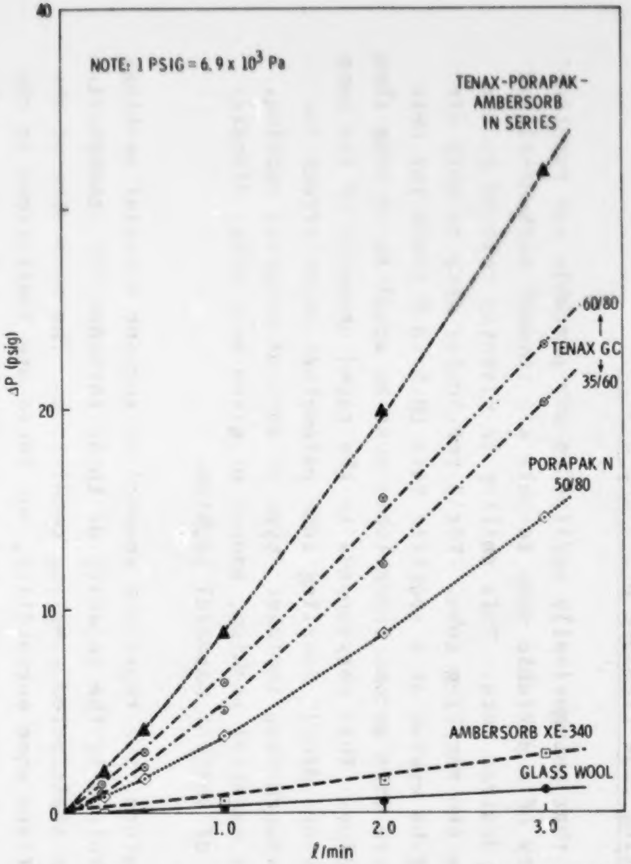


FIGURE 13. Pressure drop versus flow rates for 15 cm, 0.6 cm O.D., 4 mm I.D. glass sampling tubes filled with sorbent materials.

and have fewer contamination and reactivity problems.

Evaluations of Sampling Tube Pressure Drops and Design

One limitation that automatically applies to any portable air sampling system is the ability of a portable pump to pull air through sorbent-filled sampling tubes at a desired rate. This ability is directly related to the pressure drop across the sampling tube. For a particular pump to pull air through a sampling tube system at a specific rate (0.5 to 3 l/min for this project), the pressure drop across these tubes must be equal to or less than a certain maximum value. This corresponds to the rated capacity of the pump at a particular pressure drop. Sampling tube parameters which affect the magnitude of the pressure drop include: type of sorbent material packing, mesh size of sorbent material packing, amount of glass wool plug, diameter of tube, and amount of sorbent material packing.

Of these parameters, the types and amounts of sorbent material packings will be mainly determined by the capacity of these sorbents for atmospheric pollutants under the anticipated sampling conditions. The mesh size of the sorbent materials offers some versatility, but there are limitations to the mesh sizes available. The amount of glass wool used to contain the sorbent material within the tube can be a critical factor in determining the pressure drop, so that care should be taken to ensure that the minimum amount of glass wool is used. In larger diameter tubing, a method of restraining the glass wool plug may be necessary when minimal amounts of glass wool are used. Tapering the ends of the tube or inserting a stainless steel screen are two possible ways to secure the glass wool plugs.

The experimental parameter that offers the most flexibility in determining the pressure drop is the tube diameter. The only restriction on the diameter of the tube is the necessity to achieve rapid and uniform heating of the sorbent bed during the thermal desorption process. This becomes increasingly difficult with increasing sampling tube diameter.

The pressure drops across sampling tubes of various shapes, diameters, and sorbent beddings were measured using a differential pressure gauge. Flow rates were set by using a Brooks Model 5841 thermal mass flow sensor/controller. An example of the type of data generated during these pressure studies is given in Table 12 and depicted in Figure 13.

These pressure drop studies led to the conclusion that a 10-mm diameter

TABLE 12

Pressure Drop Data for Glass Sampling Tubes[a] (psig)

Flow rate (ℓ/min)	Tenax GC 60/80 mesh 0.1953 g w/34.3 mg glass wool	Tenax GC 35/60 mesh 0.2014 g w/34.3 mg glass wool	Porapak N 50/80 mesh 0.2018 g w/38.9 mg glass wool	Ambersorb XE-340 (not sieved) 0.1964 g w/36.1 mg glass wool	Glass tube without sorbent w/36.2 mg glass	Tenax GC (35/60), Porapak N, and Ambersorb XE-340 in series
3	23.2	20.3	14.8	3.0	1.1 to 1.2	31.8
2	15.8	12.3	9.0	1.6	0.6	19.9
1	6.4	5.1	3.8	0.4	0.1	8.8
0.5	3.0	2.2	1.6	0.1	-	4.0
0.25	1.5	1.0	0.8	~0	-	2.0

[a] 6 in. long, 1/4 in. O.D., 4 mm I.D.

Other conditions

Transfer lines only at 3 ℓ/min show ~0 psig pressure drop.
Inlet pressure: 62 psig; downstream pressure: 9 psig.

TABLE 13

Adsorbent Properties Chart

Adsorbent	Temp. limit (°C)	Cond. temp. (°C)	Des. temp. (°C)	Chemical composition	Major thermal decomposition products	Background level	ΔP[a] (psig)	Capacity	Desorption	Range of utility (in terms of δ_m)
Tenax-GC (35/60 mesh)	400	320	300	2,6-Diphenyl-p-phenylene Oxide	Alkyl Benzene Styrene Benzene Alkyl Phenols	GOOD (none detected above system background)	160	Should efficiently trap intermediately (& less) volatile compounds with slightly less affinity for polar compounds.	Very amenable to thermal desorption for intermediately (& all higher) volatile compounds.	~850 to >2800
Porapak R (50/80 mesh)	250	235	150 to 220	n-Vinyl Pyrrolidone	Vinyl Pyrrolidone Pyrrolidone Pyrrilidiene	After conditioning at 235°C, background upon desorbing is: POOR @ 220°C (well above syst. background) FAIR @ 150°C (slightly above syst. background)	~1.1[b]	Should efficiently trap intermediately (& less) volatile compounds with slightly greater affinity for polar compounds.	Very amenable to thermal desorption for intermediately (& all higher) volatile compounds.	~750 to ~1500
Porapak N (50/80 mesh)	190	175	150	n-Vinyl Pyrrolidone	Vinyl Pyrrolidone Pyrrolidone Pyrrilidiene	POOR (well above system background)	1.1	Should efficiently trap intermediately (& less) volatile compounds with slightly greater affinity for polar compounds.	Very amenable to thermal desorption for intermediately (& all higher) volatile compounds.	~750 to ~1500
Ambersorb® XE-340	>400	320	300	Carbonized Styrene-divinyl Benzene	none observed (after conditioning at 350°C + observing on GC/MS)	GOOD (none detected above system background)	0.6	Should efficiently trap highly (& all less) volatile compounds with greater affinity for polar compounds.	Questionable amenability to thermal desorption for all but highly volatile hydrocarbons.	~450 to ~750
SKC Activated Charcoal	>400	320	300	Carbonized Organics	none observed	GOOD (none detected above system background)	~0.6[b]	Should efficiently trap highly (& all less) volatile compounds with much greater affinity for polar compounds.	Questionable amenability to thermal desorption for all but highly volatile hydrocarbons	~350 to ~600

[a] Pressure drop across tapered tubes containing 1.0 g of adsorbent at a 3 liter/min flow rate.

[b] Estimated.

represents a reasonable compromise between the requirement to have the smallest possible diameter for efficient thermal desorption and yet maintain an acceptable pressure drop across sorbent-filled tubes. Two designs, straight and tapered, with 10-mm cross sections, were evaluated taking into account the desirable design features of the miniature collection system. Although the tapered tubes had higher pressure drops than the straight tubes, the difference was not significant. Furthermore, the tapered design offered advantages for the containment of the sorbent, since smaller amounts of glass wool can be used with no "blowouts" of sorbent material. Finally, lighter, less expensive (one-quarter inch) fittings can be used with the tapered tubes, which is an important factor in the design and construction of a miniature collector. The specifications for the cartridge design determined to be most desirable is given in Figure 14, along with a sketch of a sampling tube.

Evaluation of Sorbent Package

Five sorbent materials have been evaluated to determine their basic properties, including special abilities and potential problems.

Table 13 is a compilation of the major sorbent material properties evaluated. Along with the name of the adsorbent is included:

- The manufacturer's stated temperature limit (or >400° C).
- The temperature used for sorbent conditioning.
- The temperature used for sorbent desorption.
- Some of the major thermal decomposition products.
- A qualitative description of the background to be expected from the sorbent material.
- The pressure drop across tapered tubes containing 1.0 g of adsorbent at a 3 l/min flow rate.
- A qualitative description of the type of compounds that will potentially be quantitatively trapped by the adsorbent (capacity $\geq$480 l/g).
- A qualitative description of the type of compounds that will potentially be quantitatively thermally desorbed for analysis.
- The range of utility based on δ_m (described previously).

Of these five sorbents, a combination of three has been selected for use in the miniature collection system. These three sorbents are listed below along with the major reasons for their selection.

Tenax-GC. The only high-temperature (400° C) adsorbent available which allows the quantitative thermal desorption of low volatility organic compounds.

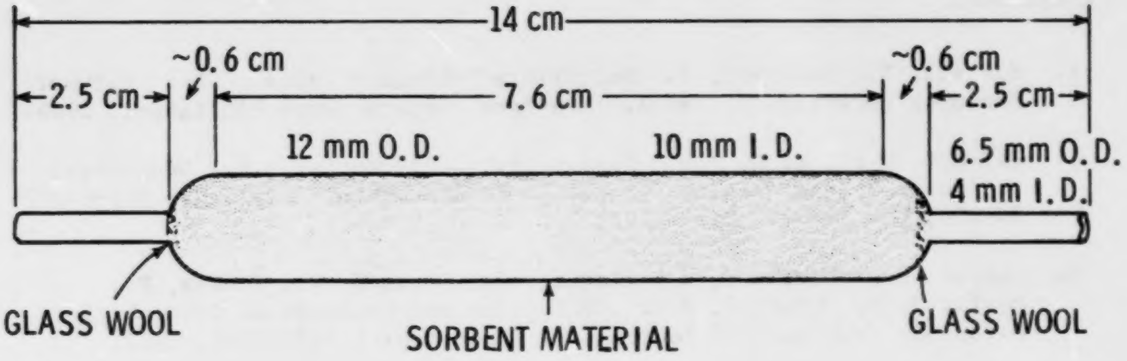


FIGURE 14. Specifications for tapered sampling tube design.

Porapak R. One of the highest-capacity polymeric absorbents with a reasonable background level (better than Porapak N) and with an overlap in range of utility (δ_m) with Tenax-GC.

Ambersorb XE-340. Less difficulty anticipated with the desorption of compounds of intermediate volatility, fewer detrimental effects by water and reactivity with collected samples than with charcoal. Also, its range of utility (δ_m) leaves the smallest gap between polymeric and carbonaceous adsorbents in the types of compounds collected.

These sorbent materials will be packed into three separate tapered glass tubes for sampling, with flow being directed either in series or in parallel. If sampling is done with the sorbent tubes in series, the arrangement will be Tenax-GC at the air intake, Ambersorb XE-340 at the air exhaust to the pump, and Porapak R in the middle. In terms of total range of utility (δ_m) of the sorbent package, it should quantitatively trap and desorb compounds ranging from ∿450 to >2,800 (δ_m) with a possible "qualitative only" gap at ∿750 (δ_m).

ACKNOWLEDGEMENT

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Discussion

SCHEIDE: Gene Scheide, Environmetrics. What was the temperature used in the thermal preparation of your adsorbent material?

BROOKS: It varies with sorbent material. Of course, it is based on what the upper temperature limit is. We used about 350 degrees Centigrade for the Tenax, for the Ambersorb and the charcoal.

We used about 175° C for the Porapak N, and about 240° C for the Porapak R. Again, these are related to what their upper thermal limit is.

I should say we will be evaluating these sorbents in the second year against 20 possible and probable carcinogenic compounds that have been identified as being of interest.

SPENGLER: I understand you have not used all of these in the field, yet. The Tenax is currently being used by Lawrence Berkeley Labs on indoor-outdoor measurements, to look at organics.

But we would like to relate someone else's experience: that of Peter Mueller from Environmental Research and Technology who also used a Tenax collector in ambient conditions. He related that they had some serious problems with blank contaminations with the Tenax, and they were totally frustrated with the its use.

I don't know if you have any comments on what would cause that, but he said that oftentimes the blanks would have more material on them than the exposed Tenax. They are disenchanted with it.

MEIER: Gene Meier, EPA, Las Vegas. The problem with Tenax traps is aging. As your trap ages, it degrades, and you can't hold a trap for more than 3 weeks; otherwise, you get a significant hydrocarbon background from two sources--either just contamination from the normal environment on your Tenax, or also it can be the composition of the Tenax itself.

If you look at your gas chromatogram, you will see a typical hydrocarbon response, along with the chromatogram of the various alkanes as they break down off the Tenax itself. That's why I would like to see some of the data on the Ambersorbs, because we have done some work at Las Vegas--not our lab personally, but the people at the University--and the Ambersorb seems to be a lot cleaner than the Tenax in trapping all the organics from water samples, which I would expect would hold true here.

BROOKS: The reason that we are using three different materials is because we have to cover the range of compounds. You might have problems recovering a lot of the heavier, less volatile materials--if you were just using Ambersorb.

MEIER: Have you actually physically collected the samples and tested, or are these hypothetical results?

BROOKS: We have done a limited amount of sampling with test compounds. Right now, in the second year, we will be working with the actual 20 compounds that we have selected to determine what the collection and adsorption efficiencies are.

MEIER: The people out at Research Triangle Park have been using the Tenax traps for their monitoring program and have been quite successful in trapping a wide range of hydrocarbons, including your heavier molecules.

BROOKS: With Tenax, right, but I am saying that with Ambersorb, you are not going to get them back.

MEIER: I realize the differences there, but I am saying that you work in a whole series and one of the questions I am asking is why is the Tenax acceptable, while you are looking for the three solvents?

BROOKS: Because when you are talking about sampling, say, at a liter-per-minute for 8 hours, you are going to get significant breakthrough of the higher volatility compounds--they will not be trapped.

MEIER: Well, they have been collecting 100 liter samples on 5/8-inch diameter and I would say about 4 inches long tubes, and have been quite successful. They use it in the quality assurance program where they spike their traps before they go out in the field, so they can verify when they have a breakthrough.

BROOKS: I doubt that they are successful for the really highly volatile compounds. Let me say just one other thing. We do have first annual reports available on two contracts that relate to this type of sampling and that will be out very shortly.

MAGE: I just might add from my own personal experience that so much depends on the method of preparation. One batch of Tenax may not be the same as the other. There is a lot to be done to maintain quality.

Adapting Commercial Voltammetric Sensors to Personal Monitoring Applications

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Interscan Corporation
Chatsworth, California

Of recent concern to industrial hygienists and safety engineers is the exposure of workers to harmful levels of noxious gases and vapors. Apart from the survey type or fixed-station monitor, there is a need for an inexpensive but accurate personal monitor with real time indication--one that is wearable without being burdensome. The one proven analytical technique meeting these requirements is the electrochemical voltammetric method of instrumental analysis.

PRINCIPLE OF OPERATION

The voltammetric method differs from other instrumental methods of gas analysis, such as the coulometric, conductimetric, or colorimetric techniques, which require that the sample gas react with chemical reagents. In the voltammetric technique, sample gas is electro-oxidized (or electroreduced) directly at an electrode. This makes it possible to design a simple and practical portable monitor using a dry technique.

The voltammetric sensor operates under diffusion-controlled conditions. The gas sample is drawn through the sensor, passing over an electrocatalytic sensing electrode of the gas diffusion type. Some of the gas molecules diffuse into and are adsorbed on the electrode, where they are electrochemically oxidized or reduced (depending on the sensor) at an appropriate electrode potential. This electrochemical reaction results in an electric current, directly proportional to the gas concentration.

To understand the concept of a diffusion-controlled reaction, picture a single pore within the porous surface of the sensing electrode. Within each such pore, a thin film of electrolyte constitutes a microscopic meniscus in contact with the sample gas, creating a three-phase junction of gas, liquid, and solid (electrode surface), shown schematically in Figure 1. The total electro-oxidation reaction of a sample gas includes dissolution of gaseous molecules in this thin liquid film, diffusion or mass transfer of the dissolved gas through the film, adsorption of the gas on the electrode, and transfer of the electron charge to the metal surface. The reaction becomes diffusion-limited when the gas is consumed at a greater rate than can be replenished at the reaction site; that is, when the charge transfer reaction is faster than the mass transfer reaction. The limiting diffusion current is linearily proportional to the gas concentration according to the simplified equation

$$i = \frac{nFDAC}{L} = KC$$

where i is the limiting diffusion current in amps, F is the Faraday constant (96,500 coulombs), A is the reaction interface area in cm^2, n is the number of electrons per mole reactant, L is the diffusion gradient in cm within the thin liquid film, C is the concentration ($moles/cm^3$) of gas molecules dissolved in the thin liquid film, and D is the diffusion coefficient (cm^2/sec) of the gas. To be an analytical device having linear readout with gas concentration, the voltammetric sensor must be biased so that the electrode reaction occurs within the diffusion-limited region of the voltammetric curve. This is illustrated in Figure 2, showing typical voltammetric curves for several gases. Electrochemical current is plotted as ordinate, and the sensing electrode potential as abscissa, relative to the reversible hydrogen electrode (RHE) at zero potential. Increasing oxidation potential (more positive values--Stockholm-Gibbs convention) is towards the right. Oxidation current is arbitrarily chosen as positive.

Taking SO_2 as an example, no reaction occurs until a minimum oxidation potential is reached at a, at which point current begins to flow, increasing until it attains a limiting value at b. Since the region b to c represents the diffusion-limited region of the current, the sensing electrode in the SO_2 sensor is held at an oxidation potential of V_1 volts. This is accomplished by applying the appropriate bias voltage to the sensing electrode relative to the reference counterelectrode. Similar voltammetric curves are shown for H_2S and CO oxidation. NO_2 is unique in that it exhibits both oxidation and reduction characteristics.

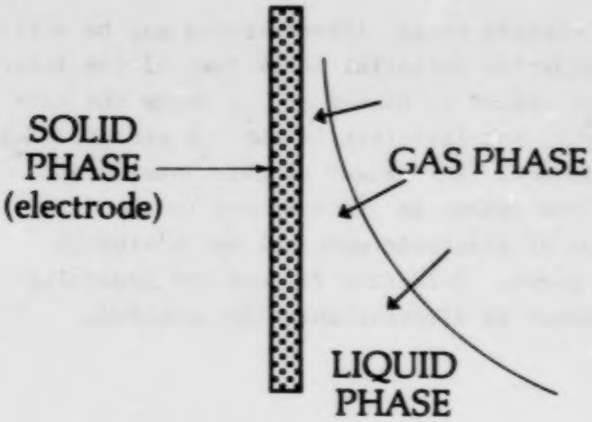
SOLID
PHASE
(electrode)
GAS PHASE
LIQUID
PHASE

FIGURE 1. Electrode-electrolyte interface.

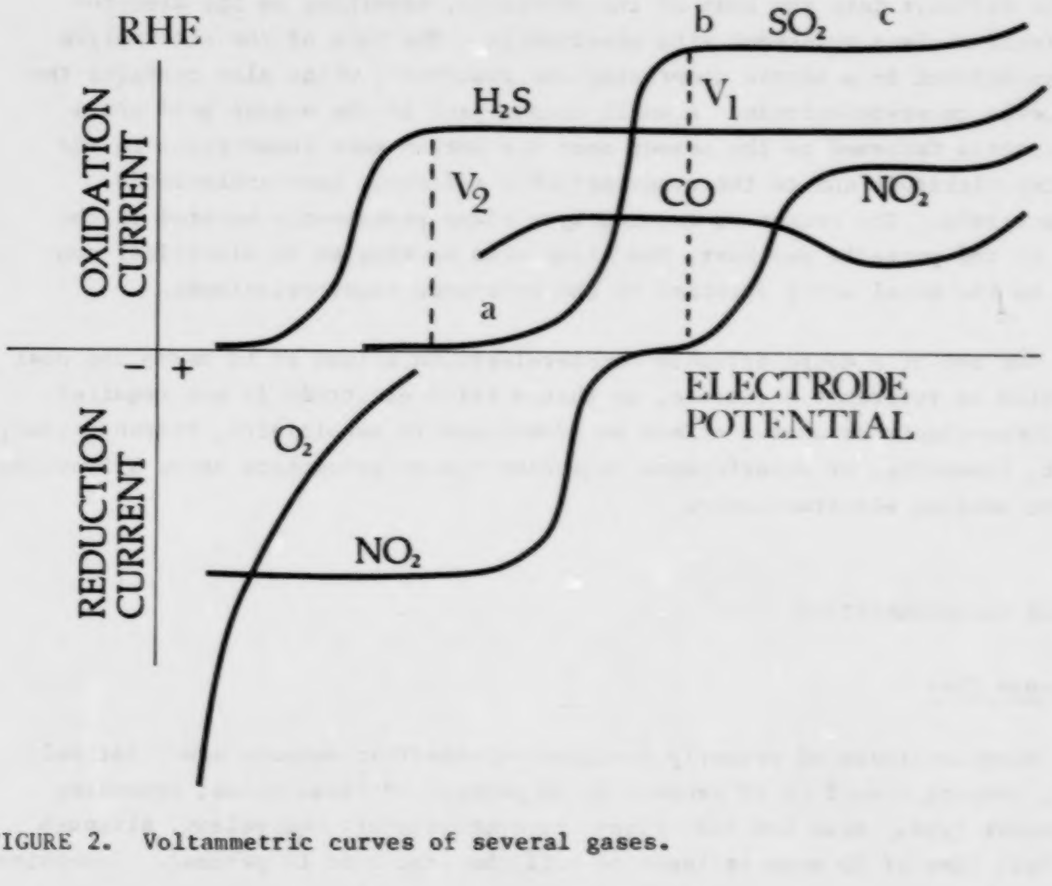

FIGURE 2. Voltammetric curves of several gases.

These curves also show that in certain cases, interferences may be eliminated by biasing the sensor at an oxidation potential below that of the interfering gas. For instance, if the H_2S sensor is biased at V_2, below the oxidation potential for SO_2, then SO_2 will not interfere in the H_2S sensor. H_2S will, however, interfere in an SO_2 sensor. The extent of this interference depends upon the specific output of the sensor in its response to the interfering gas. In certain cases, choice of electrode material may virtually eliminate interference from certain gases. Selective filters are generally used when a potential interferent cannot be electrochemically scrubbed.

SENSOR DESCRIPTION

Figure 3 is a schematic representation of a voltammetric sensor used in present commercial survey monitors. Sample air, drawn into the sensor by a pump, streams over the backside of the sensing electrode. A portion of the sample diffuses into the body of the electrode, adsorbing on its electrocatalytic surface moistened with electrolyte. The bulk of the electrolyte is immobilized in a matrix comprising the reservoir, which also contains the reference counterelectrode. A small banana jack in the sensor head and a metal strip fastened to the sensor near its bottom make connections to the sensing electrode and to the nonpolarizable reference counterelectrode, respectively. The sensor is secured by a clamp permanently mounted to the base of the portable analyzer, the clamp also serving as an electrical contact to the metal strip attached to the reference counterelectrode.

The use of a nonpolarizable counterelectrode allows it to serve the dual function as reference electrode, so that a third electrode is not required. The three-electrode sensor offers no advantages in sensitivity, response time, drift, linearity, or interference rejection--these parameters being a function of the sensing electrode only.

SENSOR CHARACTERISTICS

Response Time

Response times of properly designed voltammetric sensors are relatively fast, ranging from 3 to 20 seconds to 90 percent of final value, depending on sensor type. Rise and fall times are approximately equivalent, although the fall time of CO sensors tends to tail the last 5 to 10 percent. Excessive

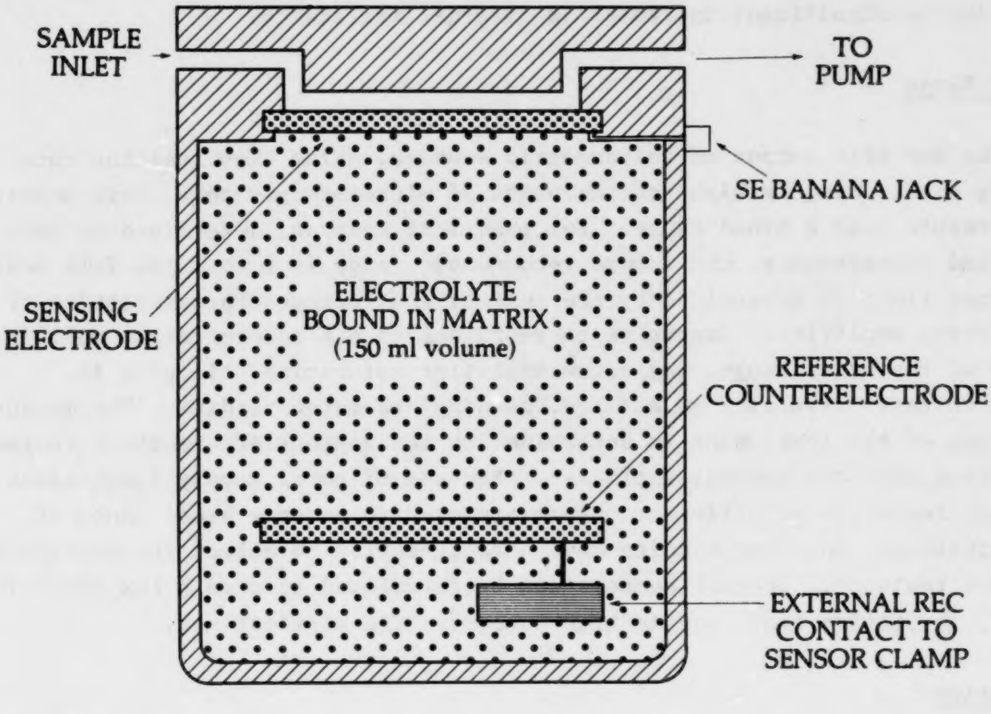
SAMPLE INLET
TO PUMP
SE BANANA JACK
ELECTROLYTE BOUND IN MATRIX (150 ml volume)
SENSING ELECTRODE
REFERENCE COUNTERELECTRODE
EXTERNAL REC CONTACT TO SENSOR CLAMP

FIGURE 3. Voltammetric sensor in portable monitor.

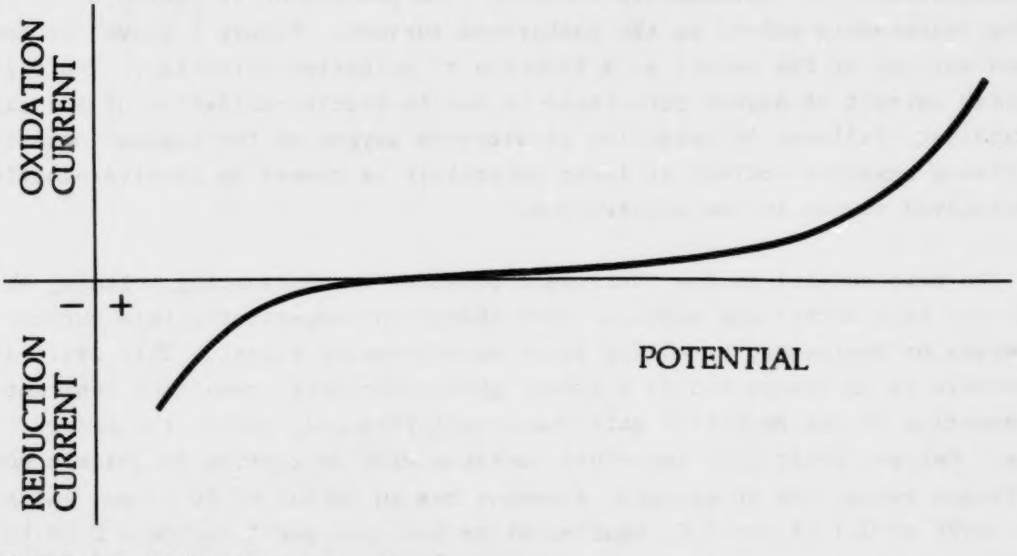

FIGURE 4. Background current of sensor.

drying out of some sensors, particularly the CO type, increases the response time, due to significant increases in internal resistance.

Sensor Range

The specific output of voltammetric sensors, using high reaction rate sensing electrodes, is high--on the order of microamps-per-ppm. This permits measurements over a broad range. For practical reasons, determined by zero drift and interference, the lowest recommended range is 0 to 1 ppm full scale. The upper limit is determined by the current and voltage characteristics of the current amplifier. Excessive current, due to gas concentration well in excess of the meter range, may cause amplifier saturation, clipping the output voltage--resulting in a fixed, meaningless meter reading. The measuring range of the instrument is determined by the appropriate feedback resistor associated with the current amplifier. Because of power supply limitations, feedback resistors of different values are used to cover a broad range of concentration. Multirange units have a range switch to select the particular feedback resistor. Special sensors can be formulated to give a low specific output, permitting their use in high-concentration applications.

Zero Drift

A key performance parameter of a practical sensor is its zero drift characteristic. In voltammetric sensors, this phenomenon is caused strictly by the temperature effect on the background current. Figure 4 shows the background current of the sensor as a function of oxidation potential. The rising positive current at higher potentials is due to electro-oxidation of the electrocatalyst, followed by oxidation of water to oxygen at the highest potentials. The rising negative current at lower potentials is caused by electroreduction of dissolved oxygen in the electrolyte.

The zero control in the instrument provides a compensating voltage, which nulls out this background signal. With change in temperature, this current increases or decreases, resulting in an uncompensated signal. This drift is measurable in microamps and is a sensor phenomenon only, remaining constant irrespective of the amplifier gain characteristics and, hence, the meter range. Percent drift must therefore increase with decreasing full-scale concentration range. As an example, a sensor has an output of 10 μA/ppm and a zero drift of 0.1 μA per ° C, equivalent to 0.01 ppm per ° C. On a 0 to 10 ppm range, this corresponds to a change of 0.05 ppm for a 5° C change in temperature, giving a zero drift of 0.5 percent of full scale. This corresponds to 5 percent drift on the 0 to 1 ppm range and 0.5 percent drift on the 0 to 100 ppm range.

Sample Flow Rate

Sensor output is flow dependent at flow rates below 2 liters-per-minute, as illustrated in Figure 5. This is not a pressure effect, as demonstrated by data obtained by pushing the sample through the sensor from a pressurized cylinder, or pulling it through using the internal pump and a sample bag. This flow effect is a result of the rapid consumption of gas at the high reaction rate sensing electrode. As the flow rate is decreased, there is less tendency for new gas molecules to replenish those consumed at the electrode; i.e., the flow rate becomes less and less sufficient to fully sustain the reaction. Figure 5 shows that a decrease of flow rate from 940 to 740 ml/minute decreases the sensor output by 5 percent.

Actually, the flow rate effect is an advantage because no purge of the sensor is required. One merely shuts off the pump for zeroing. The portable Interscan analyzers have a constant flow pump so that the flow rate is fixed, independent of the state of battery charge. Calibration with a sample bag ensures that the same flow rate will be used for the sample measurements.

PERSONAL MONITORING

The electrochemical voltammetric technique is highly suited to real time air quality monitoring and integrated exposure measurement. It is probably one of the few available techniques offering a combination of small size, low cost, minimal maintenance, and accurate linear output. The scaling down in size from a portable monitor to a personal monitor requires no basic development effort, but is rather one of design engineering. A large reduction in sensor volume can be accomplished with only a relatively small reduction in area of the active elements--the electrodes.

The sensor in the portable, survey-type monitor has been reduced from a volume of 24 in^3 to 1 in^3 for the personal monitor. The total volume of the personal monitor is less than 20 in^3 compared with 525 in^3 for the portable monitor. This drastic reduction in size in done by reducing the size of the reservoir. The trade-off is the necessity for the frequent addition of water to the personal monitor reservoir. (No addition of water is required in the sensor shown in Figure 3, which has a sufficiently large reservoir to give a sensor life of a year or more of normal use.)

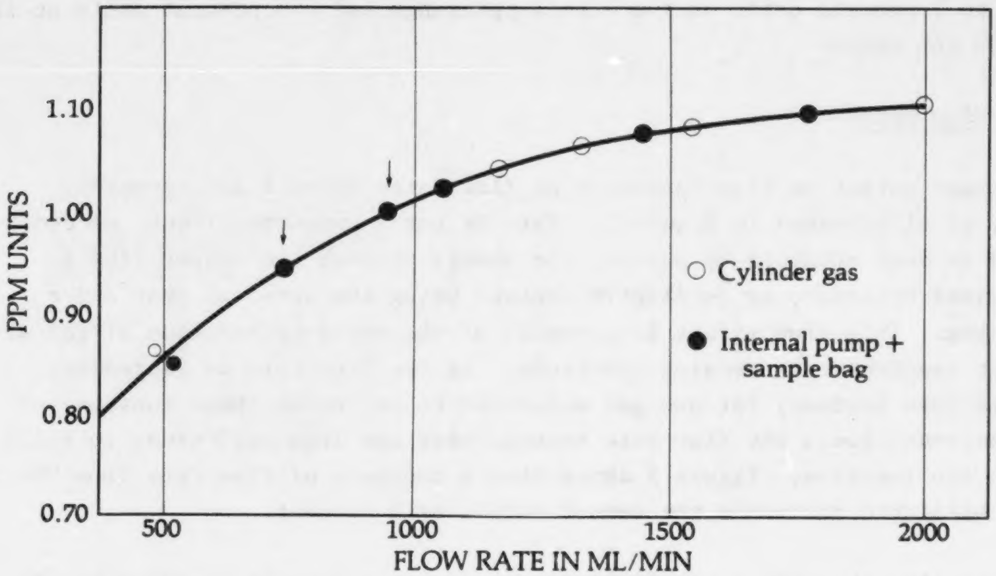

FIGURE 5. Effect of sample flow rate on sensor output.

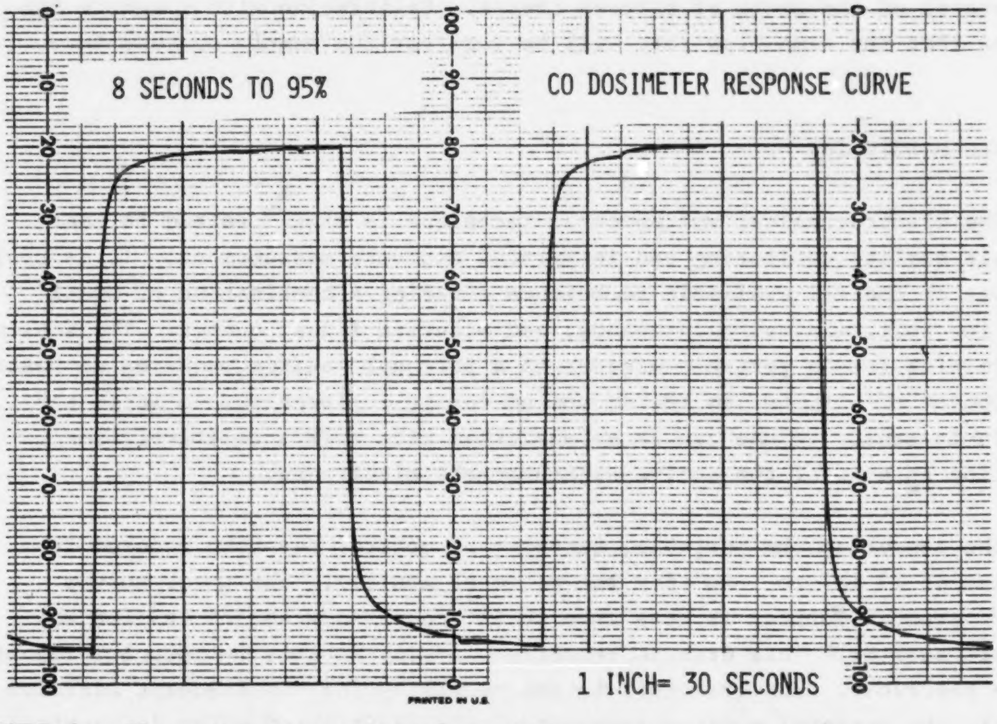

FIGURE 6. CO response in personal monitor.

Such reduction of size does not affect sensor performance. Figure 6 shows the response curve of the 1 cubic inch sensor in the CO personal monitor. Rise and fall times are rapid. Rise time is 8 seconds to 95 percent (chart speed shown is 1 inch equals 30 seconds).

PERSONAL DOSIMETERS

The voltammetric technique is particularly suitable for personal dosimeters which give an accumulated exposure over a time period. Using coulometric or electronic integrators, the total dosage in ppm-hours is obtained in a separate read-back unit. Read-back may be done at the end of an 8-hour shift, and the time-weighted average (TWA) calculated from the ppm-hours. If desired, read-back can be done at any time during a given period to identify the existence of high-dosage periods.

The disadvantage of this approach is that in many cases the read-back reading is an after-the-fact event, the wearer of the dosimeter already having been exposed to a TWA greatly in excess of the threshold limit value (TLV). Even though some dosimeters have an alarm indicator, it is only for indicating the ppm level at a given moment. A more practical device would be a dosimeter capable of being set to alarm at a TWA equivalent to the TLV. This concept has been developed, and is presently being used by a major steel manufacturer as an area monitor equipped with a TLV alarm. The electronics necessary to accomplish this can be packaged in a pocket-sized dosimeter. The availability of low-current logic components permit their usage in battery-powered circuits.

Figure 7 shows a block diagram of a personal dosimeter using this new concept. Shown are the more standard components such as reference voltage, zero and span circuits, amplifier, power supply, and low-battery indicator. A plug-in meter is used for calibration and ppm level measurement. The block diagram entitled TWA & ALARM CIRCUITRY represents the logic package designed to accomplish the TLV alarm. This is detailed in Figure 8.

The analog output voltage is converted to a digital format. A clock (square wave oscillator) regulates the feeding of information through the gate into memory storage. If and when the TLV is exceeded, a visual (LED) and audible (buzzer) alarm is actuated. The TLV is set at the factory, specific for that type of dosimeter. A second circuit permits a second alarm to activate, based on exceeding the Short-Term Exposure Limit (STEL). This is indicated by a different color LED and the buzzer.

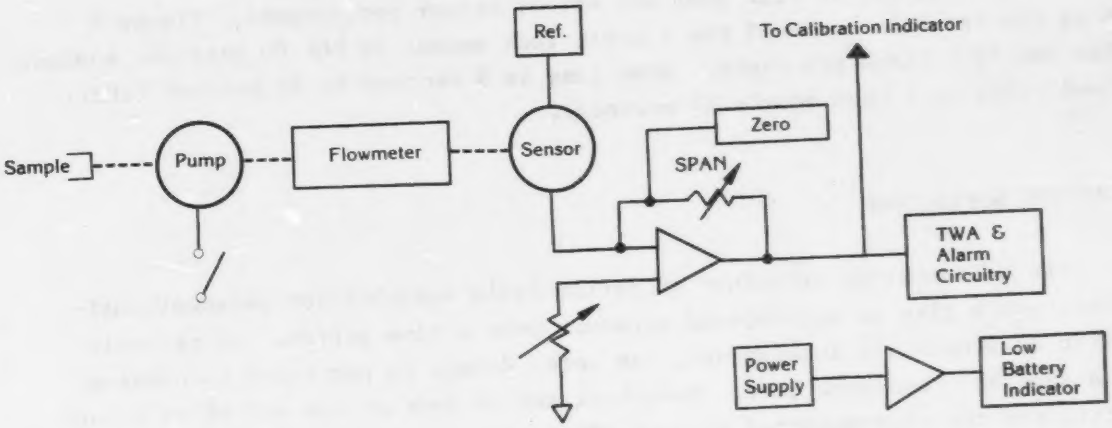
Ref.
To Calibration Indicator
Zero
Sample
Pump
Flowmeter
Sensor
SPAN
TWA & Alarm Circuitry
Power Supply
Low Battery Indicator

FIGURE 7. Block diagram of TLV alarm dosimeter.

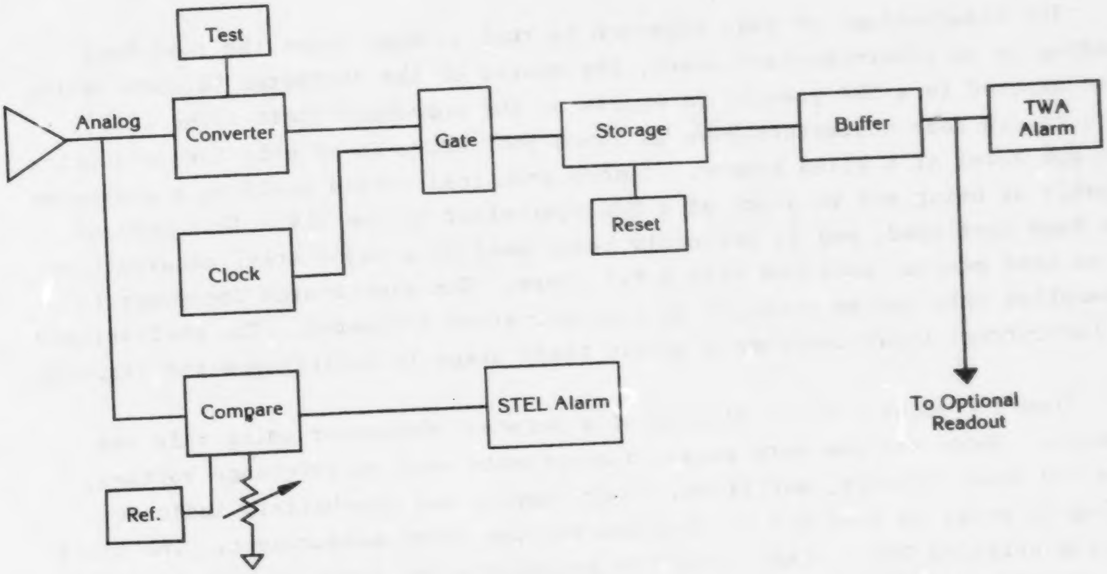
Test
Analog
Converter
Gate
Storage
Buffer
TWA Alarm
Reset
Clock
Compare
STEL Alarm
To Optional Readout
Ref.

FIGURE 8. Block diagram of TWA integrator.

An important feature of this dosimeter is the TEST circuit, which allows the user to check the operation of the TLV alarm. By flipping a switch, a signal is generated, which is designed to actuate the alarm in a given specific time, such as 30 seconds. The timing of the alarm is precise, within ± 1 second. The timing is so precise that the test should be repeated three or four times to be certain that the timepiece is being read correctly. (The RESET control is used to clear the memory.) If the alarm is actuated too soon or too late, relative to the 30 ± 1 seconds, the unit is faulty. This simple test, performed in the dosimeter itself, gives an excellent quick check for reliability.

The concept of a TLV alarm dosimeter has obvious advantages. No auxiliary read-back unit is required--the dosimeter is complete in itself. A reset button in the dosimeter allows its transfer from one worker to another during a shift, without the necessity of going to a separate erasing unit. Although an optional TWA unit will become available, there is the practical question as to its need. The main purpose in determining the ppm-hours of exposure, or the TWA, is to prevent a worker from being exposed to a dosage in excess of the TLV. If such is the case, then it seems that a logical way to do this is with a TLV alarm dosimeter.

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Discussion

PETROVICK: You illustrated a slide there where you have the electrolytes bound within a matrix. Could you give me an idea why you used a matrix and what its particular features are in that design?

SHAW: Well, I am an old battery man besides being a fuel cell man, and I don't see the logic of taking the sensor and putting in free acid, because if the electrodes which are rupturable diaphragms are ruptured, you have got free acid all over the instrumentation.

I used to meet electronic engineers and when they would look at such devices they would exclaim: "Oh, gee, we would never put that into our instrumentation--having an acid electrolyte in there." They don't stop to think: they do the same thing with NiCd batteries all the time. It has got strong alkali like the material you clean up a toilet with. It's the same type of alkali; it is that strong--23 percent potassium hydroxide. But it isn't sitting around there loosely, slushing around. It is in a matrix, bound up. So, we simply make the sensor the same way.

Solid Sorbent for Acrolein and Formaldehyde in Air

Avram Gold, Ph.D., Thomas J. Smith, Ph.D., Christoph E. Dube, and John J. Cafarella
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INTRODUCTION

Acrolein and formaldehyde are toxic and irritating volatile aldehydes of increasing interest in industrial hygiene and environmental settings. Outdoor sources of acrolein are combustion and diesel exhaust, while indoor sources may be cooking and smoking. Formaldehyde exposure in residences from particle board and blown-in urea-formaldehyde foam have recently generated concern.

Current sampling methods for both aldehydes (7,8) involve the use of liquid-filled impingers and are not particularly well-suited to personal sampling. Additionally, the acrolein analysis must be performed within several hours after sampling, and the effect of storage on formaldehyde samples is unknown. Studies on stability of formaldehyde solutions of low concentration, however, strongly suggest that storage will present problems (11). Since our initial interest in the aldehydes was for inclusion of a sampler in a package to be used by Boston firefighters on-the-job, we desired a solid sorbent which would have a large specific capacity and provide stability for stored samples.

DISCUSSION

Activated molecular sieves have been used extensively in industry to purify gas streams (1,6) and, unlike currently available porous polymers, have large capacities for adsorbates--20 to 30 percent by weight. Despite the clearly indicated potential for air sampling, molecular sieves have not found much application for this purpose. We therefore undertook an investigation to determine the suitability of molecular sieves for sampling low molecular weight aldehydes in air. For this study, 13X sieves were chosen because large pore size would ensure efficient mass transfer. Sieves were ground to 12/30 mesh and activated by heating slowly to 400° C under vacuum and maintaining temperature and vacuum overnight. Because acrolein is more toxic than formaldehyde and the problem of obtaining constant concentrations in air much more straightforward, verification of sieves as a sampling medium for acrolein received priority.

Acrolein

Since some labile compounds react on sieves even at ambient temperatures (2,9,10), efforts were initially directed at determining the yield of recovery from sieves. When known amounts of acrolein were loaded onto sieves as vapor, recovery by desorption with chilled distilled water (sieves added to water) was quantitative: 97 ± 11 percent for 3 to 8 μg acrolein/g sieves, 90 ± 7 percent for 60 to 200 μg/g. Analysis of desorbate was performed by gas chromatography on Tenax-GC with a flame ionization detector. Sample tubes loaded with equal volumes of vapor, stored in a refrigerator, and analyzed serially over 4 weeks showed no losses.

The performance of sieves was assessed by determining the breakthrough characteristics of acrolein. We determined that the Theory of Statistical Moments (TSM) (3-5) would describe the behavior of acrolein on sieves and extrapolated breakthrough performance from moderate to low concentrations by TSM. In this manner, problems inherent in working with low concentrations of a reactive compound were avoided. The apparatus in Figure 1, shown in a configuration for breakthrough testing, was capable of producing constant concentrations in the range 400 to 3,000 ppm for periods of up to 4 hours. Typical breakthrough data obtained with 1 g of sieves in a 10 mm I.D. sampling tube at a sampling rate of 1 l/min are given in Figure 2.

As the solid curves indicate, breakthrough is satisfactorily described by curves constructed from the σ's (standard deviation) and $t_{0.5}$'s (breakthrough time of 50 percent of input concentration) derived from the data. Table 1, Column 3, indicates that the relative standard deviation σ^* ($=\sigma/t_{0.5}$) is ~ 0.2 and invariant with concentration as required by TSM.

Figure 3 shows the dynamic adsorption isotherm calculated from the break-

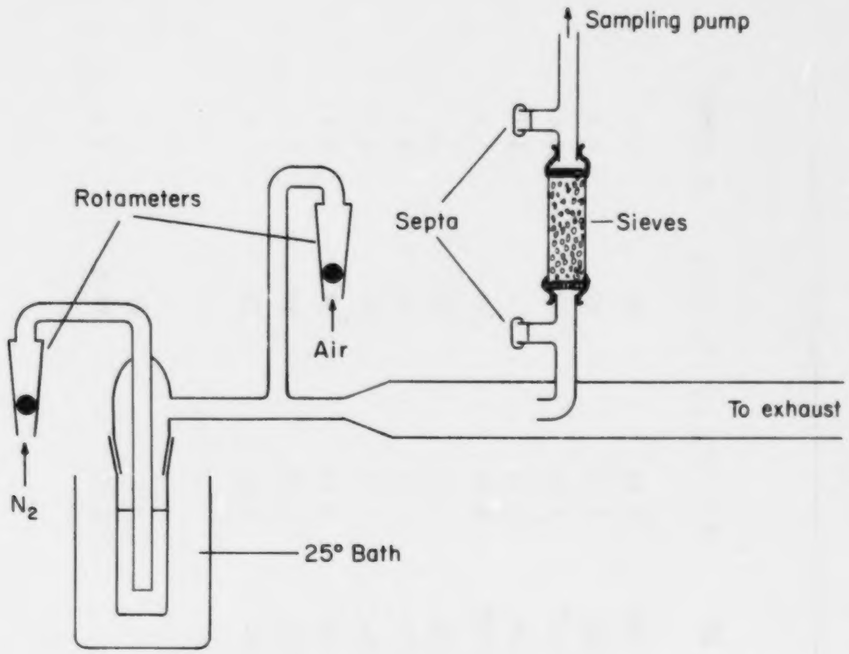
Sampling pump
Rotameters
Septa
Sieves
Air
To exhaust
N2
25° Bath

FIGURE 1. Dynamic dilution apparatus.

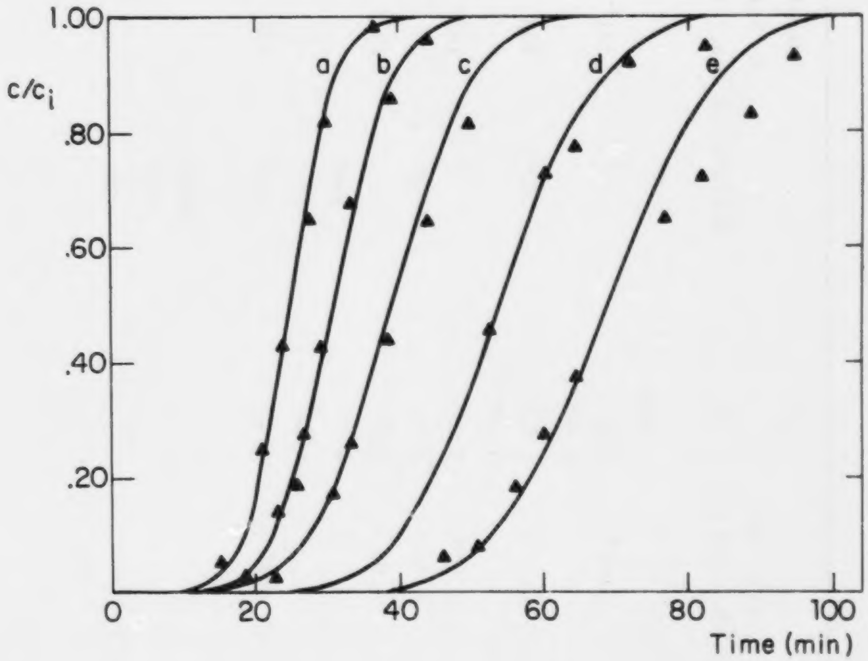

FIGURE 2. Representative breakthrough experiments for the following input concentrations: a) 6.31 mg/l, b) 4.68 mg/l, c) 3.08 mg/l, d) 2.79 mg/l, e) 1.66 mg/l.

TABLE 1

Breakthrough Data for Acrolein and Water on 13X Sieves

				acrolein				
	c_i, mg/L			A, mg/g				
Gravimetric	Desorption	GC	Gravimetric	Desorption	GC	$\sigma^* = \sigma/t_{0.5}$	$t_{0.5}$, min	F, L/min
		0.903[a]			76[a]	0.18	84	1.1
	1.66[a]	2.45		121[a]	178	0.18	69	1.1
		1.96[a]			147[a]	0.15	67	1.1
2.79[a]	2.73	2.25	169[a]	166	136	0.21	54	1.1
		3.08[a]			127[a]	0.24	39	1.1
	3.22[a]	3.68		148[a]	17C	0.20	46	1.1
3.53[a]	3.39	3.52	179[a]		179	0.21	43	1.1
	4.68	5.55		151[a]	178	0.21	31	1.1
4.81[a]		5.11	166[a]		176	0.19	32	1.1
5.08[a]		4.24	174[a]		146	0.39	33	1.1
6.31[a]	6.94	6.42	179[a]	197	182	0.21	25	1.1
			water					
21.3			260			0.18	22	1.1
5.6			230			0.29	18.3	2.0

[a] Data used in least squares fit to Langmuir isotherm. Accuracy of results was assumed to be gravimetry > desorption > GC.

through data (Table 1) by a least squares fit to the best Langmuir isotherm. The fit is quite good, with a correlation coefficient of 0.94 and standard error of estimate ± 19 percent. In addition, the calculated saturation capacity (dashed line, Figure 3) of 236 mg/g is in good agreement with the experimental value of 226 mg/g determined in static experiments.

With the assumption from TSM of concentration independent σ^*, the breakthrough curve for any concentration can be constructed from the corresponding $t_{0.5}$ determined from the isotherm by the relation

$$t_{0.5} = \frac{a}{c_i} \times \frac{w}{F}$$

where a = capacity, mg/g
c_i = input, concentration, mg/l
w = weight of sieve bed, g
F = flow rate, l/min
and $\sigma = \sigma^* \times t_{0.5}$

Calculated 5 percent breakthrough times for various acrolein concentrations sampled in dry air at 1 l/min with 1 g sieve beds are given in Table 2. Since 2 μg acrolein/g sieves can be readily determined by GC analysis, the sensitivity for acrolein in dry air is 0.01 ppm for an 80-liter sample.

Because water will displace acrolein from the sieves, the effect of humidity on acrolein breakthrough had to be defined. Breakthrough of 1,500 ppm acrolein at 30 percent relative humidity superimposed on the water breakthrough curve is shown in Figure 4. Figure 5 shows results of a similar experiment at 100 percent relative humidity. The acrolein elutes from the sieve bed with the water front in the form of a GC peak, having a variance similar to the water breakthrough curve and a concentration maximum at approximately $t_{0.5}$ of water. At 100 percent relative humidity, 5 percent breakthrough occurs in ~8 min. With a sensitivity of 2 μg acrolein/g sieves, a concentration of 0.1 ppm should be detectable in an 8-liter sample on 1 g of sieves. Since the capacity of sieves for water is constant to very low relative humidities, sample volume and therefore sensitivity will increase directly in proportion to decrease in relative humidity.

Formaldehyde

Formaldehyde is more difficult to handle. To date, the recovery of

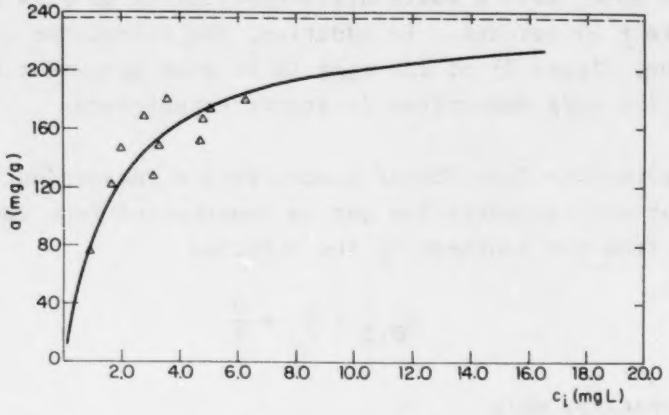

FIGURE 3. Dynamic adsorption isotherm of acrolein at 21° C.

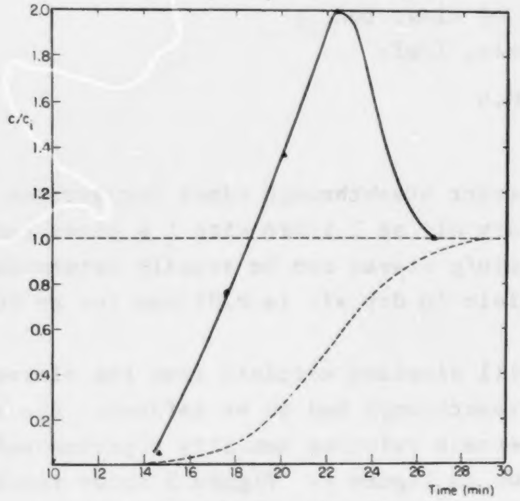

FIGURE 4. Acrolein breakthrough, 30 percent relative humidity.

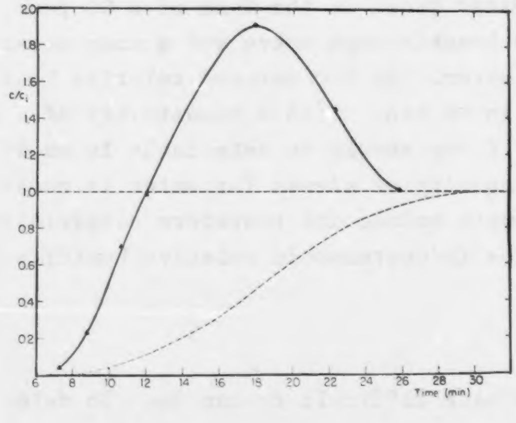

FIGURE 5. Acrolein breakthrough, 100 percent relative humidity.

TABLE 2

Breakthrough Times of 5 Percent of Acrolein Input Concentration in Dry Air

c_i (mg/l)	$t_{0.05}$ (min)
4.57	20
2.29	43
0.229	72
0.023	82
0.0023	82
0.0002	82

formaldehyde from sieves has been established when it is loaded as vapor from formalin headspace. Relatively high concentrations were used so that analysis of desorption solutions could be performed by GC on Carbowax 20 M with a flame ionization detector. The chromatograms of formalin and the headspace show two peaks in addition to methanol (present as a preservative). The major peak, preparatively chromatographed and collected in water, gave a chromophore with chromotropic acid and was assumed to be monomeric formaldehyde (and/or the hemiacetal with methanol). This peak was used as a standard for determination of formaldehyde in desorption solutions. The presence of the monomeric aldehyde in headspace was qualitatively demonstrated by observing the formaldehyde carbonyl absorbance bands in the UV on bubbling headspace into heptane in a sample cuvette.

Recovery of formaldehyde from sieves was determined by comparing total formaldehyde content of distilled water through which a known volume of diluted headspace had been bubbled with that in desorbate from sieves loaded with an equal volume of diluted headspace. For loadings of 100 to 200 μg formaldehyde/g sieves, recovery was 98 ± 5 percent; for 0.9 to 1.1 mg/g, 108 ± 5 percent. It was also determined that formaldehyde in desorbate could be analyzed colorimetrically with chromotropic acid, but only with desorption volumes ≥ 10 ml/g sieves. More concentrated desorbate gave irregular color development with yellow interference. For a 10-ml desorption volume and the sensitivity reported in Reference 8 for the final colorimetric solution, 0.2 ppm formaldehyde could be detected in an 8-liter sample on 1 g sieves at 100 percent relative humidity. We have assumed that breakthrough characteristics of formaldehyde will be similar to those of acrolein; however, work is currently in progress to describe breakthrough behavior.

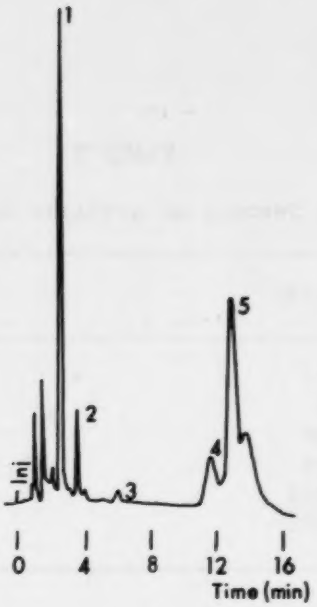

FIGURE 6. Gas chromatogram of a 2.5-liter field sample collected over 12 min at a sampling rate of 208 ml/min. The following concentrations were calculated on the basis of a comparison of peak heights with those of standard solutions: 1) methanol, 110 ppm; 2) acetaldehyde, 10 ppm; 3) ethanol, 3 ppm; 4) acrolein, 16 ppm; 5) acetone, 66 ppm.

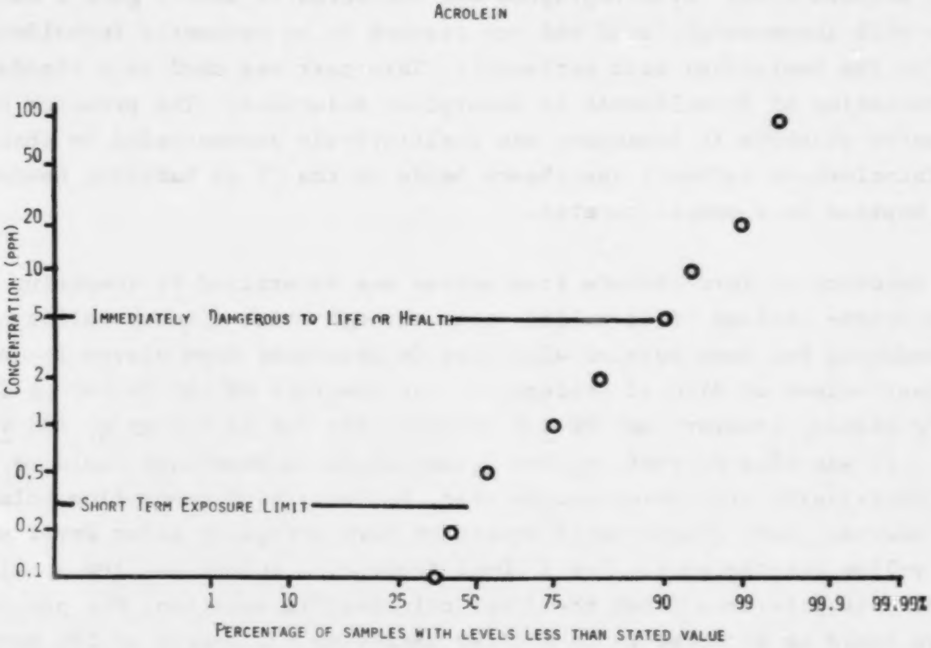

FIGURE 7. Frequency distribution of acrolein concentrations at fires, total 118 samples.

Field Measurements

Molecular sieve sampling tubes were contained in a sampling package deployed on the rescue squads of the Boston Fire Department. A gas chromatogram typical of the sample desorbates is shown in Figure 6. Formaldehyde did not elute from Tenax-GC, but its presence was confirmed by chromotropic acid analysis of the desorbate. To our knowledge, these data are the first confirmation of the presence of acrolein at urban residential fires. The distribution of acrolein concentrations in fire samples, shown in Figure 7, indicates that acrolein exposures are of concern as a potential hazard. Formaldehyde was not present in sufficient concentration to justify allocation of technician time for routine analysis. Analyses were performed on a spot basis on samples which indicated severe exposure to other contaminants. Maximum recorded formaldehyde exposure was 11 ppm.

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Discussion

DEBBRECHT: I would like to just make one comment and possibly a suggestion. The one comment is: I think you are very justified in watching out for the volatile fume that obviously you became aware of. You had to put these materials on your molecular sieve when the vapor condenses to a liquid form.

I don't know how well known this fact is, but one runs into the same problem with charcoal tubes in industrial hygiene work. It makes a difference between your efficiencies and recovery.

The second thing is that certainly the flame ionization has extreme importance to formaldehyde. One possibility is using the technique that is currently available on a GC system for carbon monoxide, which is also not detected by flame. And that is to convert the carbon monoxide to methane at the GC separation, when that occurs, using a nickel and hydrogen atmosphere. This should certainly work with formaldehyde and at least give you methane-sensitive formaldehyde.

GOLD: Yes, there are several possibilities. They are interesting possibilities, and Dr. Lin here has suggested, for example, a photo ionization detector. We do not have that capability and would not have it in the near future.

DEBBRECHT: I don't think the photo ionization detector has enough energy to get the formaldehyde; I might be wrong.

GOLD: I have not had any personal experience with that. I understand that it is high enough in energy, so that it would attach hydrocarbons, if the formaldehyde is present as an aldehyde, when it enters the detector--we have some evidence that it is. We are very worried about the form of the formaldehyde because of the fact that if it appears in a gas stream as a monomer--or anything that has a molecular diameter smaller than the pores of the sieves--it won't be collected; it will pass right through. So, we were very worried about whether we had monomer or polymer. We had some interesting experiences with the effluents from permeation tubes, using paraformaldehyde.

Also, there is a possibility perhaps of doing the analysis by high performance liquid chromatography. One has a very good chromophore in the dinitrophenolhydrazine group. The concentration of the desorbate which would occur in a prechromatographic step on some sub-packing could also be used. I don't think there is any doubt that the method could be improved considerably.

I also have talked to other people who have had problems with the chromotrophic acid determinations. We used it, because at least as far as our verification experiments were concerned, we knew we were dealing with formaldehyde or something like formaldehyde.

I can't remember whether I have said that we do have some evidence that the formaldehyde in the headspace of the analyzer contains at least some of the aldehyde, because we bubble the headspace vapor into heptane in a UV spectrophotometer, and in fact, we're able to see the fine structure of formaldehyde in the UV.

So, at least some formaldehyde is present as monomer.

MEIER: I would caution you about extrapolating from high concentrations to low concentrations. Past experience on other studies that we have done indicate that the small amounts or irreversible adsorption that do take place on things such as molecular sieves become more and more significant as your concentration becomes less and less, and can result in errors of 100 to 200 percent or false-negative results indicating nothing is there when indeed there is.

GOLD: I guess my answer to that would be that I think that for the applications which most people would be interested in, errors are tolerable of 100 percent at really low levels, if you are talking parts-per-billion.

MEIER: If you are talking about criteria level--and I am just using a hypothetical case--of parts-per-million, and you irreversibly adsorb at that level so that you are actually getting results of zero, it becomes very significant.

GOLD: That's true. At those parts-per-million levels we are OK. We can take enough of a sample so that irreversible adsorption in the small pores, or whatever, of the sieves would not significantly impair our accuracy.

If one worries about trace analysis, that is another story, and at this point, I wouldn't care to comment.

Passive Membrane-Limited Dosimeters Using Specific Ion Electrode Analysis

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INTRODUCTION

In recent years, many workers have described systems using permeation techniques for detecting and determining toxic gases in the atmosphere. Kenneth E. Reiszner and Philip W. West (8) described a method using a silicone rubber membrane with a liquid collection medium for measuring sulfur dioxide at ambient levels (7).

Similarly, B.I. Ferber, F.D. Sharp, and P.W. Freidman at the Bureau of Mines used a silicone membrane, a liquid collecting medium, and an ion specific electrode readout for determining oxides of nitrogen (2).

Methods have been developed for vinyl chloride, carbon monoxide, nitrogen oxide, sulfur dioxide, hydrocarbons, and ammonia utilizing diffusion principles (1-8,10). This report describes the development of a system for detecting a number of inorganic gases in the air and a rapid method for determining their levels.

SYSTEM REQUIREMENTS

In designing the systems, a number of requirements were formulated as being necessary for successful performance. The membrane must be mechanically strong, uniform, and be free of reaction with solution chemistries. The

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membrane permeability must be uniform from piece to piece and slow enough to be the limiting layer; that is, free from effects of changes in flow pattern around the dosimeter. In addition, the permeability should be relatively low for water (and high for the contaminant), combined with a rapid time response for integrating peak values, and low sensitivity to temperature change. Perhaps most importantly, the membrane/solution combination should exhibit linearity with respect to both time and concentration.

The solution chemistries must be stable for 6 months before exposure, and the stoichiometrically formed products must be invariant for at least 2 days. A rapid and complete reaction to form the product is necessary to ensure proper integration--that is, maintain a zero partial pressure for the contaminant within the dosimeter. In addition, the reagent and analytical method must be selective, sensitive, and capable of covering a wide concentration range.

Theoretical Background

Although much attention has been given to a theoretical model for geometrically limited diffusion for dosimeter designs (3,5,6,9), no work has clearly outlined the theoretical design criteria for a successful membrane-limited dosimeter.

The past several years have seen a rapid advance in gas-permeable membrane technology. This technology has been applied with great success at Orion Research, Inc., in the development of a large number of gas-sensing electrodes. The use of these membranes in dosimeters, while apparently quite different, involves the same problems and theoretical analysis which were developed for the gas-sensing electrodes (9).

On exposure to an atmosphere containing the sensed species, [illegible] steady state will be attained in a short time (less than 1 minute), and steady state solutions to Fick's Law of Diffusion can be applied. Concentration gradients of a diffusing gas under steady state conditions are shown in Figure 1. There are three diffusion phases: a boundary layer outside the membrane of thickness l_B which depends on the aerodynamics of the sample atmosphere; the actual membrane whose thickness is l_M; and an internal absorption liquid. Within any phase, the concentration gradients are linear, and the flux of the diffusing species per cm^2 is given by:

$$F = \frac{D\Delta C}{l} \qquad [1]$$

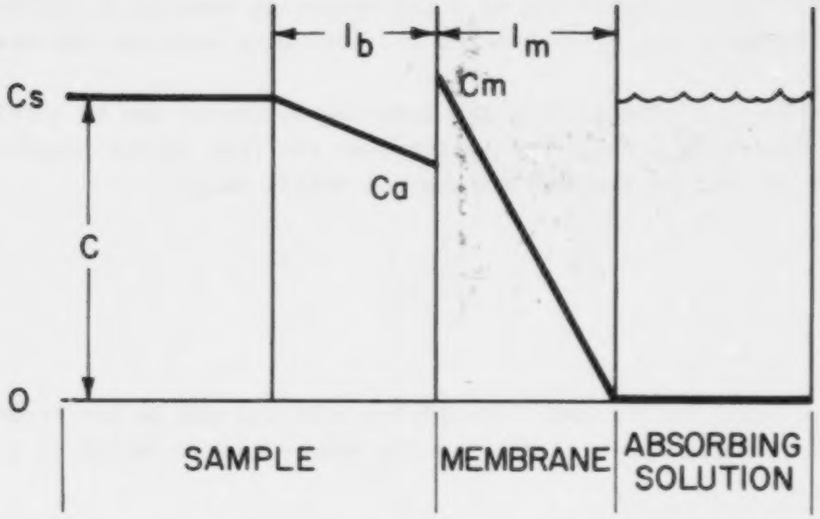

FIGURE 1. Membrane-limited diffusion model. Cs atmospheric concentration, l_b boundary layer, l_m membrane layer, Ca concentration in boundary layer at membrane surface, Cm concentration in membrane at outer surface.

where F is the flux in moles/cm^2/sec

D is the diffusion coefficient in cm^2/sec

l is the phase thickness in cm

ΔC is the concentration difference between the phase boundaries in moles/cm^3.

A concentration discontinuity may exist at the outer surface of the membrane because of the partition of the diffusing gas between air and the membrane phase. Such partition reactions are rapid for most gases, and it is permissible to assume that equilibrium exists at the interface; i.e.,

$$C_m = k\ C_a \qquad [2]$$

where C_m and C_a are the boundary concentrations of the diffusing gas in the membrane and in air, respectively, and k is the partition coefficient (i.e., the Henry's Law constant for the gas expressed in dimensionless units).

At the membrane-absorbing solution interface, the concentration of the diffusing gas is zero, since the absorbing solution is designed to contain a sufficiently high concentration of a fast-reacting species to destroy every molecule of diffusing gas which reaches the absorbing solution surface.

The overall flux of diffusing gas into the dosimeter can be obtained by combining Equations 1 and 2 and noting that the flux in the boundary layer must be equal to that in the membrane in the steady state.

$$F = \frac{D_m k}{lm + \frac{D_m k l_b}{D_a}} \qquad C_s \tag{3}$$

where D_m and D_a are the diffusion coefficients of the gas in the membrane and in the air, respectively, and C_s is the sample concentration in moles per cm^3.

If the gas reacts with the absorbing solution to produce s moles of product per mole of gas, then the final concentration of the product after an exposure time t is

$$C_p = \frac{s}{V} \int_o^t F dt \tag{4}$$

$$C_p = \frac{s}{v} \quad \frac{D_m k}{l_m + \frac{D_m k l_b}{D_a}} \int_o^t C_s dt \tag{5}$$

where V is the volume of the absorbing solution, and C_p is the concentration of the product sensed by the ion specific electrode in the absorbing solution. Thus, C_p is proportional to the integrated exposure to the reacting gas concentration C_s in the environment.

AERODYNAMIC EFFECTS

The constant of proportionality in Equation 5 includes a term involving l_b, the boundary layer thickness. In normal use, the dosimeter will be exposed to atmospheres which vary from completely static to high flow-rate situations. As a consequence of the variable rates of stirring, the effective boundary layer thickness l_b will vary. Virtually no design data are available regarding air flow patterns in the immediate neighborhood of a human subject, and exact predictions of l_b are therefore not possible. Measurements in our own laboratory, however, under static conditions yield values of l_b on the order of 10^{-1} cm. Extrapolations of published engineering data on "gas side resistance" in absorption columns suggest that l_b has a value around 10^{-2} at flow velocities of 1 mph, and that this thickness decreases rapidly with further increase in flow velocity. It was necessary, therefore, to select a membrane with appropriate values of l_m, D_m, and k, such that

$$\frac{l_m}{D_m k} > 10 \frac{l_b}{D_a} \text{ for 10 percent accuracy} \qquad [6]$$

Values of D_a for gases of intermediate molecular weight (20 to 100) in air at atmospheric pressure at room temperature are on the order of 0.1 cm^2/sec, and for the membrane, $D_m k \approx 2 \times 10^{-4}$ cm^2/sec for SO_2, NH_3, and H_2S and $l_m = 2.54 \times 10^{-2}$ cm. Thus, substituting for D_a, $D_m k$, l_m, and for l_b, the worst case static condition value of 10^{-1} cm, we have:

$$\frac{2.54 \times 10^{-3}}{2 \times 10^{-4}} > \frac{10(10^{-1})}{.1} \qquad [7]$$

thus 13>10

The condition on accuracy imposed by Equation 5 is therefore met, and dosimeters of the type proposed can operate with negligible interference from variable aerodynamic states in the environment. Laboratory tests have confirmed this result.

SOLUTION CHEMISTRY

Sulfur Dioxide System

An acid buffer assures that all sulfur dioxide is trapped on entering the solution in the form of bisulfite ion.

$$H_2O + SO_2 + NaX \rightarrow HX + NaHSO_3 \qquad [8]$$

Sulfur dioxide is complexed in such a way that an ion which can be sensed by electrode is stoichiometrically released.

Ammonia, Hydrogen Fluoride, Hydrogen Chloride

The dosimeter filling solution consists of a buffer which provides the necessary trapping pH and antibacterial action. The pH is on the acid side; this converts all ammonia entering the dosimeter into ammonium ions. An ammonium specific ion electrode using a macrotetralide antibiotic as the ion selective element is used in combination with a single junction reference electrode to complete the measurement cell. Similarly, hydrogen fluoride or hydrogen chloride are also trapped at this pH, and readout is by means of the corresponding ion specific electrode.

Hydrogen Sulfide

The approach taken is to utilize the extreme insolubility of a metal sulfide, even in the presence of an enormous excess of a strong complexing agent. Hydrogen sulfide dissolves to form hydrosulfide ion which reacts with metal ion. An electrode sensitive to the metal ion is used for the readout. This method is a so-called subtractive one, and in order to obtain a usable balance between sensitivity and range, the metal concentration of the dosimeter is set at two times the expected consumption for the point of maximum required accuracy.

Hydrogen Cyanide

The hydrogen cyanide filling solution consists of a known amount of a cyanide complex dissolved in a buffer at a high pH. At this pH, any hydrogen cyanide entering the solution will form cyanide ion. Cyanide ion further complexes the small amount of uncomplexed metal in the solution in proportion to the cyanide added. The readout cell consists of a metal ion electrode and a reference electrode.

Dosimeter Design

The prototype dosimeter units used in our experiments are shown in Figures 2A and 2B. All pieces except the O-ring were machined from linear polyethylene. The O-ring is solid Teflon.

The diffusion-limiting membrane construction is still proprietary at this time. The dosimeter is designed to contain 2 ml of absorbing solution, which leaves a small headspace. Full contact with the membrane is not necessary for accurate integration.

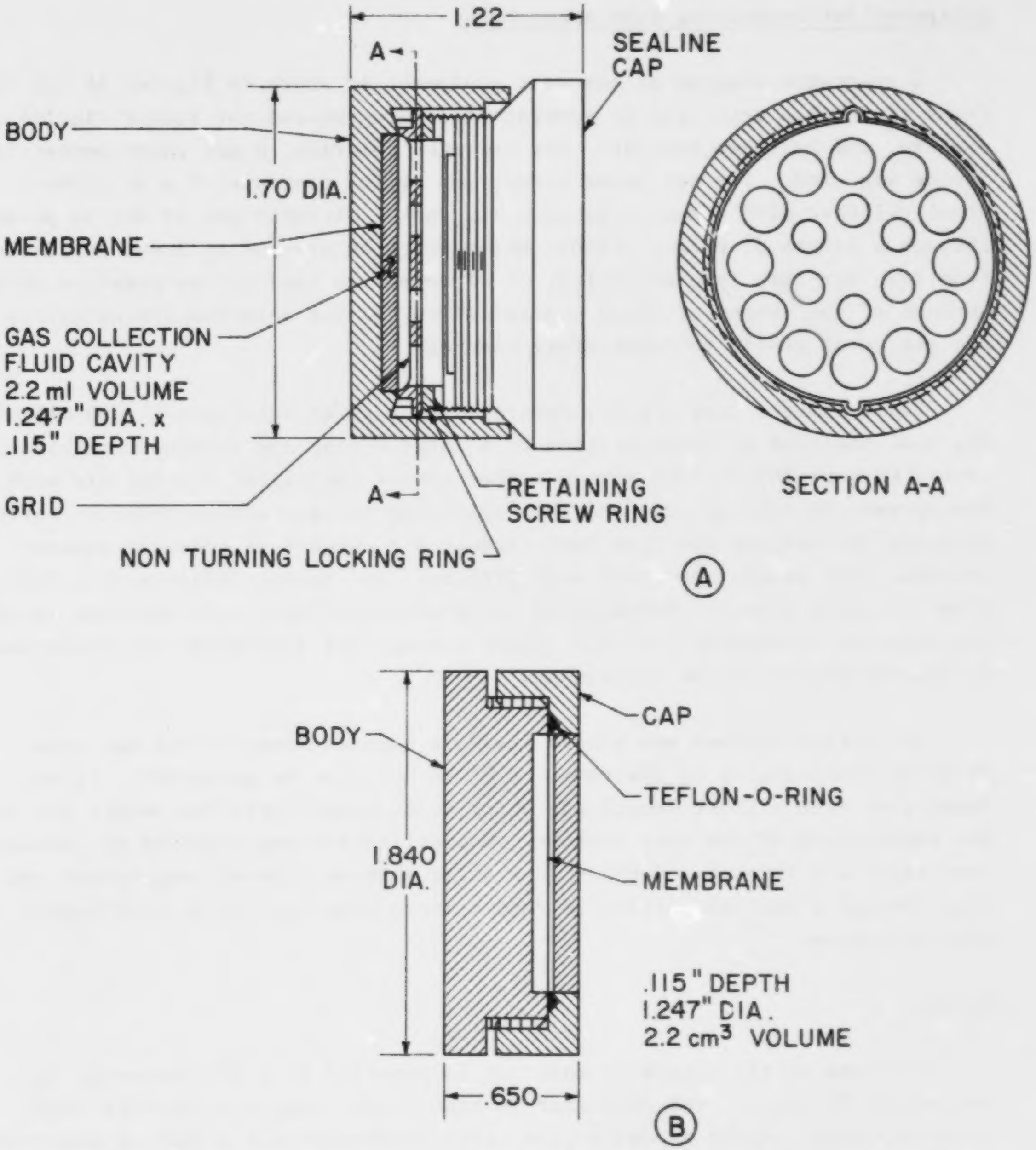
1.22
A
SEALINE CAP
BODY
1.70 DIA.
MEMBRANE
GAS COLLECTION FLUID CAVITY 2.2 ml VOLUME 1.247" DIA. x .115" DEPTH
GRID
A
RETAINING SCREW RING
NON TURNING LOCKING RING
SECTION A-A
A
BODY
CAP
TEFLON-O-RING
1.840 DIA.
MEMBRANE
.115" DEPTH
1.247" DIA.
2.2 cm3 VOLUME
.650
B

FIGURE 2. Prototype dosimeters: (A) with grid over membrane and locking no-turn washer, and (B) simplified design incorporating Teflon O-ring.

Equipment for Generating Test Atmosphere

A schematic diagram of the test equipment is shown in Figures 3A and 3B. Permeation tubes were used to generate test atmospheres for sulfur dioxide, ammonia, and hydrogen sulfide. For hydrogen chloride, a gas phase permeation device was used. The gas phase permeation device consists of a stainless steel cylinder with connections to a HCl tank. Nitrogen gas or air is passed through a length of porous Teflon tubing which enters the cylinder and exits from it. For this type of device, an air oven was used for temperature control because of the danger of water contamination and the relative insensitivity of the gas phase device to temperature changes.

The dosimeter test chamber consisted of a pyrex autoclave (2,200 ml) with the seal modified by incorporation of a large O-ring and retainer. A blending device (Figure 3B) allowed mixing either dry or humidified diluent air with the permeation tube output, and then splitting the gas stream into two parts to allow for varying the flow rate through the chamber at constant concentration. All connections were made with ball and socket joints with a thin film of vacuum grease. Bubblers on all downstream lines were provided to give the complete integrated analysis of the contaminant atmosphere concentration during the course of the experiment.

The entire chamber was placed inside a constant-temperature air oven to allow temperatures in the range of 0° to 50° C to be generated. It was found that even a short length of tubing would equilibrate the sample gas to the temperature of the test chamber. Humidification was supplied by passing compressed air through a bubbler in a water bath at reduced temperature and then through a suitable filter to remove micro droplets, or by a diffusion tube technique.

Method

A volume of the dosimeter solution is pipetted into the dosimeter body and sealed in place. The dosimeter is then stored with a protective cover until exposure. After exposure, the cover is removed and a pair of electrodes are placed into the solution. A potential is developed between the electrodes which can be measured by a specific ion electrode meter. A calibration curve is constructed (Figure 4) by adding known amounts of the ion of interest to a sample of the dosimeter filling solution. A stable reading is usually obtained in less than 1 minute. In the hydrogen sulfide system, solutions are

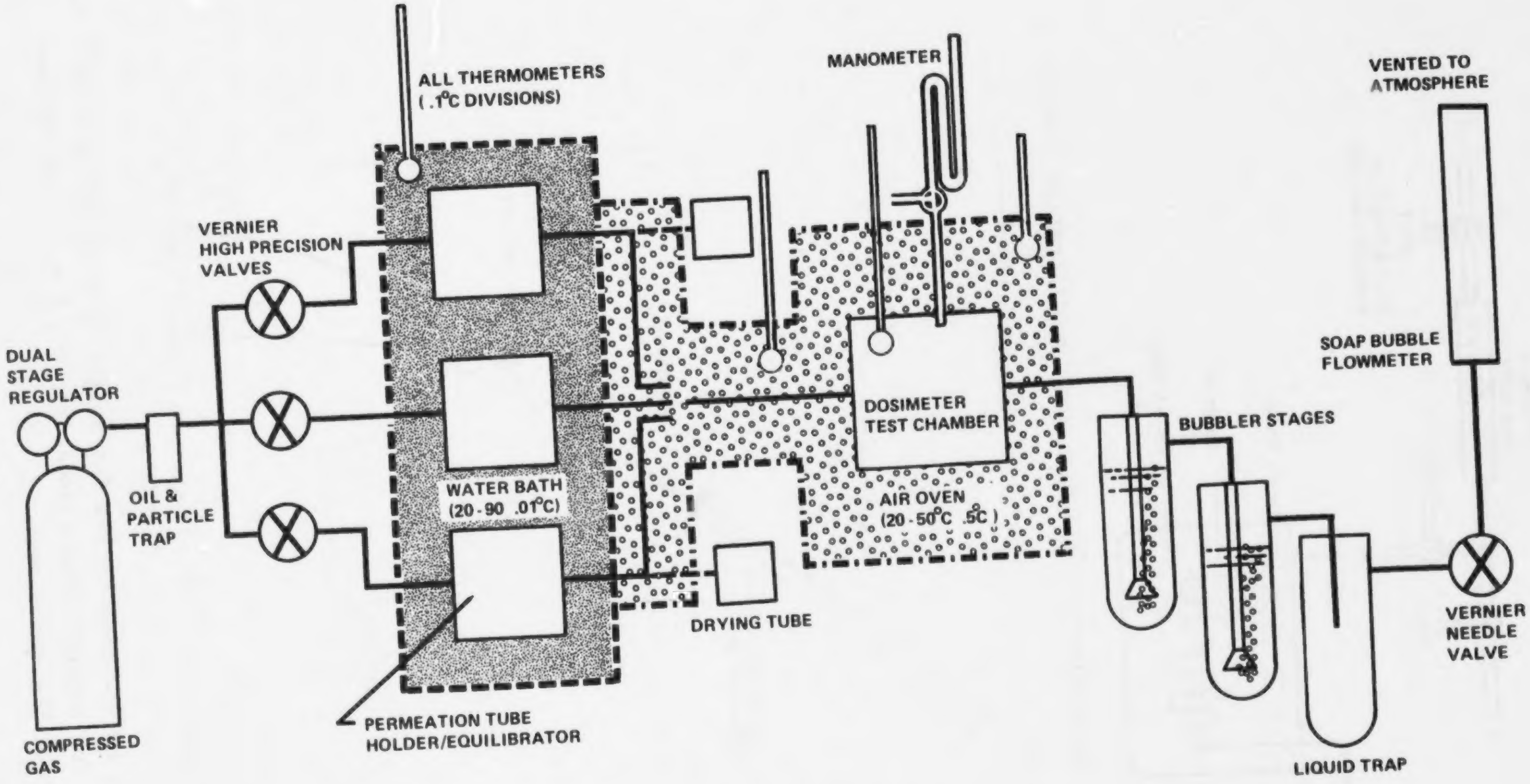
ALL THERMOMETERS
(.1°C DIVISIONS)
MANOMETER
VENTED TO ATMOSPHERE
VERNIER HIGH PRECISION VALVES
DUAL STAGE REGULATOR
SOAP BUBBLE FLOWMETER
DOSIMETER TEST CHAMBER
BUBBLER STAGES
WATER BATH (20-90 .01°C)
AIR OVEN (20-50°C .5C)
OIL & PARTICLE TRAP
DRYING TUBE
VERNIER NEEDLE VALVE
COMPRESSED GAS
PERMEATION TUBE HOLDER/EQUILIBRATOR
LIQUID TRAP

FIGURE 3A. Test apparatus--permeation tube and temperature control system.

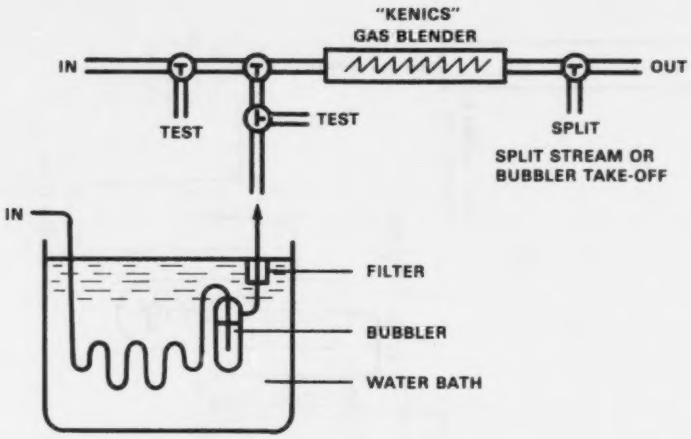
"KENICS"
GAS BLENDER
IN
TEST
TEST
OUT
SPLIT
SPLIT STREAM OR
BUBBLER TAKE-OFF
IN
FILTER
BUBBLER
WATER BATH

FIGURE 3B. Test apparatus--gas blending and humidification system.

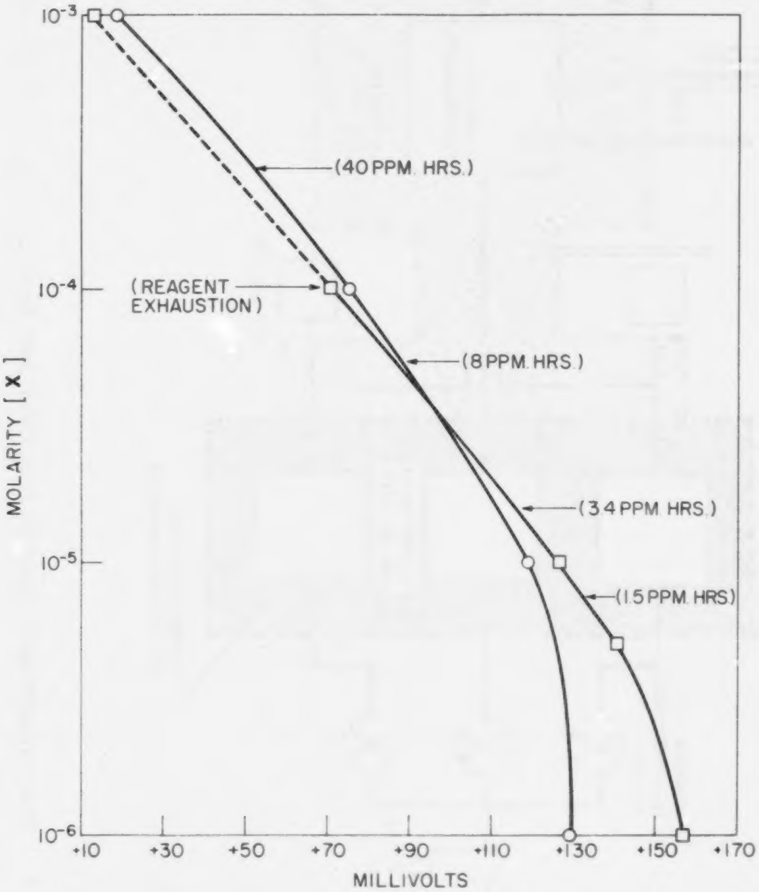

FIGURE 4. Electrode calibration curves for sulfur dioxide (O) -1 x 10^{-3} M. reagent (background for current OSHA standards); (□) 1 x 10^{-4} M. reagent (background for current EPA standards).

prepared with progressively lower concentrations by diluting the filling solution with ion buffer.

Calculations

Regular checks of permeation tube output are compared to the bubbler-integrated value to determine system holdup or leaks. Calculation of ppm exposure is based on the bubbler values corrected by the amount of gas trapped by the dosimeters and the volume of gas remaining in the chamber which does not pass through the bubblers. A permeation rate was calculated according to the formula

[9]

$$P = 1 \times 10^{9} \, \frac{(\text{ml gas [RTP]}) \times (\text{cm thickness of membrane})}{(\text{seconds exposure})\,(\text{cm}^{2}\text{ area membrane})\,(\text{cm Hg partial pressure of contaminant} - 0).}$$

Permeation rates calculated in this fashion should be constant, and independent of variations in time, concentration of exposure, and pressure. Once such permeation values have been obtained for a series of different exposure parameters, the range in these values is reduced using an average permeability to decrease the error for measurements under unknown conditions. Thus, in actual use, an average permeation value is selected for the particular gas of interest, and that value is used as a constant to convert the moles of species found in the dosimeter to ppm-hours. Dividing by the exposure time then gives the average ppm level.

RESULTS

Membrane Selection

The membrane used offers a significant advantage over the silicone membranes used by other workers. Although it is somewhat less permeable than silicone rubber membrane, we gain the advantage of less interference from windage effects. In addition to this, however, the membrane's mechanical properties allow it to be used without the individual calibration of each dosimeter. If reasonable care is used in assembly, the values obtained with a sample of the membrane are reproducible without prior calibration. All that is necessary to know is the membrane area and the solution volume. This membrane area-to-solution volume ratio is the only determinant of the concentration to be found in the dosimeter, for a given exposure time and concentration of gas. This substantial advantage allows mass production of the dosimeters without individual testing. Therefore, they can be disposable, since their manufacture is not labor intensive.

All data in this report were obtained using a fresh piece of membrane for each exposure. Thus, any variation in membrane permeability due to thickness or composition is inherent in the data.

RESULTS

Linearity

System linearity is a function of electrode slope and the permeation rate variation with concentration, time, temperature, or humidity. Typical calibration curves are shown in Figure 4 for the ion selective electrode used with the SO_2 filling solution. Figures 5A, 5B, and 5C show linearity with respect to time at various selected constant concentration levels for the ammonia, hydrogen chloride, and hydrogen sulfide systems. The regression line calculated for the hydrogen sulfide system suggests a high blank. Actually, the deviation is caused by a slight fall off in permeation rate at longer exposure times (discussed below). Each point represents a group of from four to six dosimeters.

Concentration linearity at various typical constant exposure times are shown in Figures 6A, 6B, and 6C) for the ammonia, hydrogen chloride, and hydrogen sulfide systems. The regression line for the hydrogen sulfide system was calculated using only values below 25 ppm. The high exposure levels produce a falling off in permeability, probably due to back diffusion (see discussion below).

An overall response to variation of temperature, concentration, and exposure time is shown for sulfur dioxide in Figure 7. This graph of concentration of exposure versus concentration predicted by the dosimeter shows a close correlation with the theoretical 45° slope. Reproducibility of the systems is indicated in Table 1, where statistical data are presented for each of the systems currently tested. For this table, an average permeation rate was selected based on the entire group data, and the value was then used to calculate ppm levels.

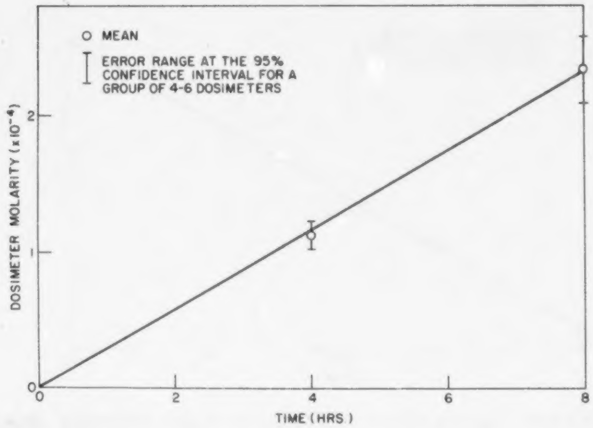

FIGURE 5A. Time linearity--exposure time versus dosimeter concentration, 5 ppm ammonia 20° C.

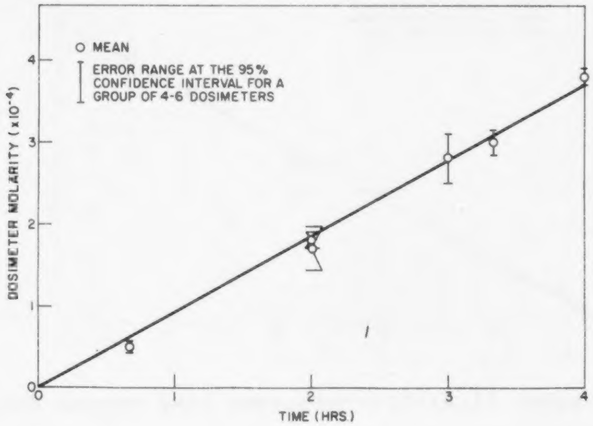

FIGURE 5B. Time linearity--exposure time versus dosimeter concentration, 10 ppm hydrogen chloride 20° C.

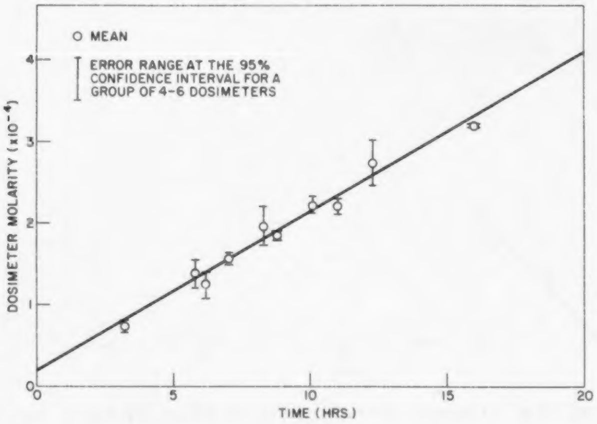

FIGURE 5C. Time linearity--exposure time versus dosimeter concentration, 20 ppm hydrogen sulfide 20° C.

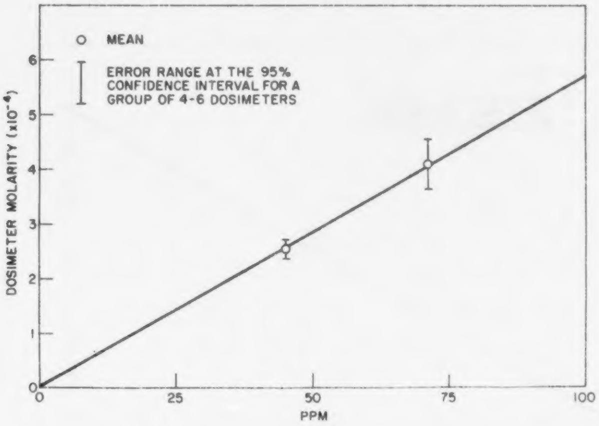

FIGURE 6A. Concentration linearity--exposure time versus dosimeter concentration, 1 hour ammonia.

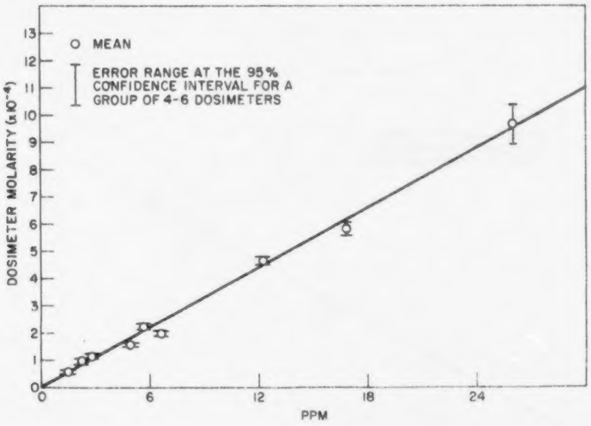

FIGURE 6B. Concentration linearity--exposure time versus dosimeter concentration, 4 hours hydrogen chloride.

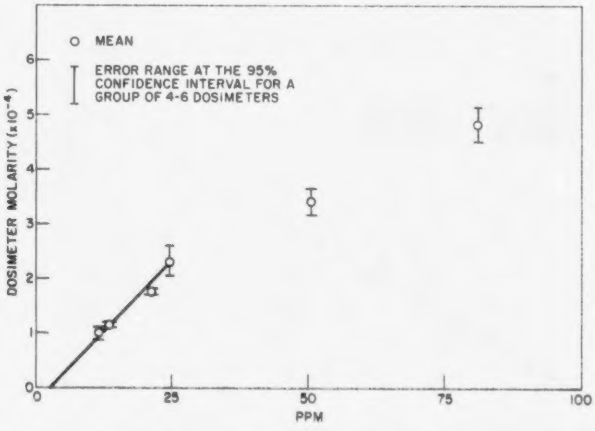

FIGURE 6C. Concentration linearity--exposure time versus dosimeter concentration, 8 hours hydrogen sulfide.

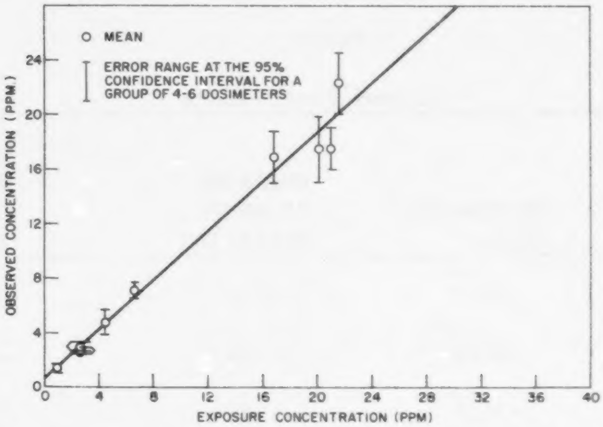

FIGURE 7. Overall system response for sulfur dioxide--test atmosphere concentration versus dosimeter calculated value using average permeation rate.

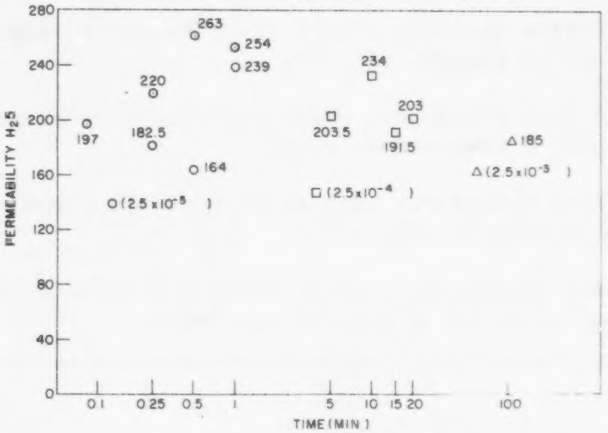

FIGURE 8. Response times for hydrogen sulfide. (O) 2.5 x 10^{-5} M. metal ion, (□) 2.5 x 10^{-4} M. metal ion, (Δ) 2.5 x 10^{-3} M. metal ion. (·) dilute buffer, ( ) concentrated buffer.

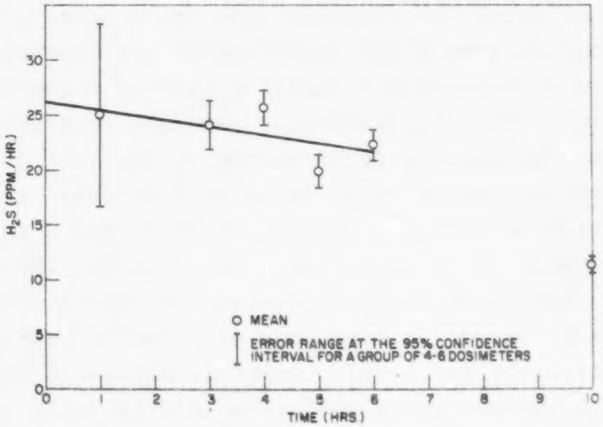

FIGURE 9. Membrane response for hydrogen sulfide--exposure time versus ppm-hour found in dosimeter.

TABLE 1

Systems Performance

DOSIMETER EXPOSURE	SYSTEMATIC ERROR	RELATIVE STANDARD DEVIATION	ERROR RANGE AT 95% CONFIDENCE LEVEL BASED ON SYSTEMATIC ERROR
SO_2 [a]:	-0.4%	5.3%	-10.8% to 10.0%
NH_3 [b]:	-3.9%	4.6%	-12.9% to 5.1%
H_2S [c]:	-3.2%	4.3%	-11.6% to 5.2%
HCl [d]:	-2.8%	4.3%	-11.1% to 5.5%

a = four exposures of five dosimeters each at 0% humidity range, 1 to 9 ppm range and 20° to 40° C temperature range.

b = four exposures of five dosimeters each at 0% humidity range, 5 to 70 ppm range and 20° to 40° C temperature range.

c = 18 exposures of five dosimeters each at 0% humidity range, 4 to 210 ppm range and 20° C temperature range.

d = 12 exposures of six dosimeters each at 0% to 45% humidity range, 1.5 to 26 ppm range and 5° C to 40° C temperature range.

Response Time

Other investigators have suggested response time for silicone rubber membrane in the range of 30 seconds to 10 minutes for various gases (1,5,8). Hydrogen sulfide was selected for response time tests since the solution used adapted itself well to adjustment for quantitating low concentrations, and the OSHA ceiling limit for H_2S requires a sampling time of under 10 minutes. A tank of 210 ppm hydrogen sulfide in nitrogen was used to generate the test atmosphere in the test chamber. A 28/15 socket on the test chamber was adapted to an earlier prototype dosimeter by means of a standard clamp. Dosimeters could be placed over the orifice and clamped in place for a set period of time. When a dosimeter was about to be placed over the orifice, the exiting gas (300 ml/min) would ensure that rapid contact between the test atmosphere and the dosimeter membrane would occur. A bleed was provided for escaping gas during exposure. For the extremely low levels, multiple exposures of the dosimeter, with a relaxation time between exposures, were used to build up a sufficient level of the sulfide in the test solution. Figure 8 illustrates the results of these tests. It should be noted that the extremely short-range tests were done with ion buffering at two concentrations. The lower values for permeation rate at short times can be related to back diffusion of H_2S from the dosimeter before reaction could occur, since higher permeation rates were obtained over the same exposure times (.1 to 1 minute) by adjusting the buffer concentration, which, by reducing complexation, raises the available metal ion concentration to that used for times from 5 to 20 minutes. This change in concentration increases the rate of reaction with hydrogen sulfide dissolving in the solution. The high gas concentration utilized, over 20 times the TLV, could readily exhaust a thin film of dilute metal ion concentration near the membrane.

Trapping Efficiency

As indicated above, for accurate integration the partial pressure of the contaminant in the dosimeter must be zero, or substantially 100 to 1,000X lower than the partial pressure of the contaminant in the atmosphere. The hydrogen sulfide system indicates some of the problems that can be encountered. With one membrane construction, a somewhat erratic and large variation in permeation rate is found, as shown in Figure 9, where exposure time versus concentration found in dosimeter is graphed for 25 ppm H_2S. The deposition of a precipitate on the interior of the membrane causes a decrease in permeation with time. Modification of the membrane construction corrected most of the change, as shown in Figure 5C, although, as pointed out above, some decrease is noted at the high end. It should be noted that the ppm-hours for typical government limits occur in the linear portion of the curve.

In addition, the hydrogen sulfide system showed some lowering of trapping efficiency with high concentration of H_2S at short exposure times, as shown in Figure 10, where the variation of permeability as a function of ppm level at constant ppm-hours is shown. High levels of H_2S probably exhaust a thin layer of buffer solution near the membrane surface and cause measurable back diffusion. The effect is minor in light of the low standard of accuracy proposed for dosimeters.

Humidity

Figure 11 shows the water loss from the dosimeters for an 8-hour exposure period at various relative humidity levels as a percentage of total solution volume. Unlike systems that use solid absorbents, one of the main limitations

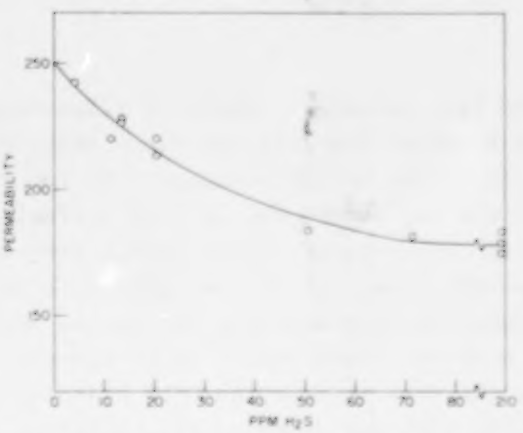

FIGURE 10. Membrane response--ppm exposure level versus membrane permeability at constant ppm-hours.

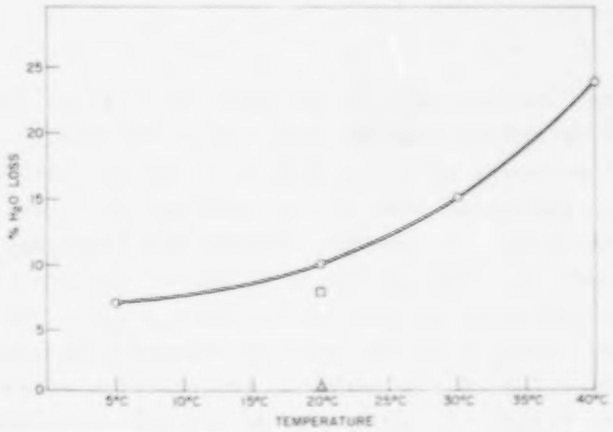

FIGURE 11. Water loss of prototype dosimeter--temperature versus percent water loss. (O) 0 percent relative humidity, (□) 40 percent relative humidity, (Δ) 100 percent relative humidity. Membrane area 8.6 cm^2, solution volume 2.2 milliliters.

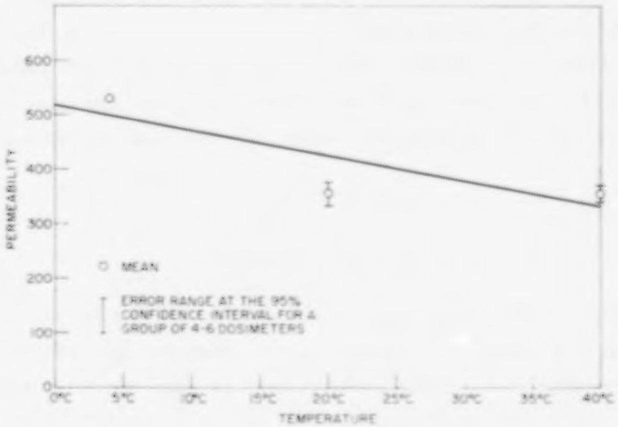

FIGURE 12. Permeability of hydrogen chloride--temperature versus permeation rate.

of the Orion system is water loss with a resultant change in dosimeter composition. Even under the most rigorous conditions, water loss is acceptable. In addition, a simple means of correction can be provided by weighing the dosimeter at the end of the exposure period and correcting the concentration by an appropriate factor.

The literature has indicated that membrane permeabilities can be affected by humidity. The hydrogen chloride dosimeter was selected as a worst case test for humidity problems with the dosimeter. The average permeability of all hydrogen chloride tests was 440. For a test at 40 percent relative humidity, the permeation rate was 415--a small difference from the average value.

It might be noted that the dosimeters themselves can generate local humidity levels in the chamber. Flow rates were kept high in most tests to keep the relative humidity below 5 percent.

Windage Effects

As noted above, the dosimeter theoretically would have very little windage effect. Tests on the sulfur dioxide system at face velocities of between 30 to 16,000 cm-per-minute showed no effects, other than slightly higher H_2O loss. A test on the hydrogen sulfide system in which dosimeters were twirled in the chamber at speeds of about 5 miles-per-hour showed no difference with those exposed to a flow of 0.001 miles-per-hour. On the other hand, dosimeters using microporous Teflon as the only diffusion-limiting layer showed erratic response in a similar test.

Dosimeters containing a grid (Figures 2A and 2B) did show about a 10 percent across-the-board decrease in permeability versus the dosimeter without such a covering (Figure 1B). This effect is ascribed to an increase in L_b, the static boundary layer (discussed above).

Temperature Effects

The literature has indicated that the effect of the permeation rate with temperature varies with the gas of interest. Reiszner (8) indicated sulfur dioxide to have a negligible temperature coefficient in silicone rubber, for example, while carbon monoxide (4) had a large temperature dependence.

The hydrogen chloride system permeation rate at constant ppm levels versus temperature is shown in Figure 12. The variation is within other

TABLE 2

Permeation Rate Variation with Temperature

FOR:	SYSTEM VALUE: Px	5° C	20° C	30° C	40° C
SO_2	330	-	285	-	370
NH_3	290	-	300	-	275
H_2S	220	-	220	-	-
HCl	440	530	>440	475	<440

experimental variables. Less data is available on other systems. Spot tests are summarized in Table 2, where permeabilities at various temperatures are shown versus the average permeability for the systems.

Interferences

The hydrogen sulfide system was designed to avoid interference by HCl. HCN would be a strong interference for this system. The H_2S dosimeter was tested in ozone at 2.5 ppm for 8 hours and nitrous oxide at 22.8 ppm for 8 hours with no change in the dosimeter solution.

The ammonium electrode is somewhat sensitive to other cationic species. Hydrazine and other low-boiling amines can pass through the membrane, but no data are available at this time on this interference level. Buffering prevents changes in the hydrogen ion concentration--the only other significant variable caused by dissolution of acid gases.

The sulfur dioxide system is sensitive to hydrogen cyanide and hydrogen sulfide gases, both of which can liberate the sensing ion. However, trapping efficiency for these gases will be very low due to the low pH of the trapping solutions relative to the pKa's.

The hydrogen chloride system would be affected by hydrogen cyanide, hydrogen sulfide, and ammonia. Hydrogen sulfide and hydrogen cyanide, however, would not be trapped efficiently by the buffer. Ammonia would be trapped as ammonium ion, which does not interfere.

The hydrogen cyanide system would have a slight interference from hydrogen sulfide. The hydrogen fluoride system has no interferences.

Storage Stability

A significant problem in designing dosimeter systems of this kind is the necessity for extremely dilute reagents and standards to remain stable for periods of 6 months or more. All the solutions used in our program have been tested in polyethylene for at least 6 months, including the standards which are generally at the 10^{-5} 10^{-4} M. level. It is hoped that some of the solutions may be stable for as long as a year. The main limitation is water loss in the dosimeter, which, due to the experimental nature of the dosimeter prototypes, has not been significantly tested. A good seal is all that is required.

Limit of Detection

The limits of detection for the current dosimeter systems are outlined in Table 3. Being of special interest to ambient air quality, an attempt was made to extend the sulfur dioxide system to its ultimate limit within the confines of the current geometry. By adjusting the internal solution concentration downward, the sensitivity was increased as shown in the calibration chart, Figure 4 above. It is possible and convenient to quantitate at the .1-ppm level for a 24-hour exposure or at the .5-ppm level for a 3-hour exposure, as suggested on the graph by the indicated levels of concentration to be expected.

The sensitivity of the SO_2 system can be increased by a factor of 2 by heating the dosimeters. Water loss at low humidities and high temperatures would put a time limitation on the device, for 24-hour exposures.

It might be possible to reduce water loss for a special application by use of a nonaqueous solvent or addition of neutral salts to the dosimeter solution.

CONCLUSIONS

A passive membrane dosimeter has been developed that requires no individual calibration, is lightweight, durable, and has no moving parts. When combined with various solution chemistries and specific ion electrodes, the dosimeter provides a system for integration of trace quantities of hydrogen sulfide, sulfur dioxide, ammonia, hydrogen cyanide, and hydrogen fluoride. The

TABLE 3

Sensitivity Limits[a]

	ppm hours
SO_2	.25[b]
	8[c]
HCl	1.6
NH_3	.8
H_2S	16[d]
	.16[e]

a) using 2.0 ml solution and a membrane area of 8.6 cm^3

b) 1×10^{-4} molar reagent

c) 1×10^{-3} molar reagent

d) 2.5×10^{-3} M. reactant

e) 2.5×10^{-5} M. reactant

analysis method is simple enough for less skilled personnel and can be done in a few minutes. The basic method can be extended to carbon dioxide and other gases amenable to electrode or other methods of analysis.

Exposure tests for various concentration, time, humidity, flow, and temperature conditions have been performed on hydrogen sulfide, sulfur dioxide, ammonia, and hydrogen chloride with results more accurate and sensitive than the current monitoring procedures required in government standards.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the work of other past and present Orion

staff members: Martin Frant, who originated the concept and developed many of the chemistries; James Ross, who provided the theoretical work on diffusion; Jon Soderberg, responsible for development of the hydrogen sulfide and sulfur dioxide systems; and Nelson Perry, who patiently carried out the test program for the other gases and provided the graphs for this manuscript.

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Discussion

SCHEIDE: Do you see any advantages that you would have on using this liquid solution collecting medium as opposed to a solid collector?

AMASS: We could use a solid collector. We just felt that from the point of view of analysis, it would be easier. We were looking, possibly, even at having field people do this work rather than having to train personnel to do it.

Personal Monitoring by Means of Gas Permeation

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There is an obvious need for personal monitors that are suitable for determining exposures to toxic agents in residential areas as well as in the workplace. For such broad applications, convenience and low costs, together with sensitivity, accuracy, and reliability, are prime requirements. Passive monitors are especially attractive because they can be produced at a relatively low cost and are the ultimate in simplicity. Passive devices for sample collection employing gas permeation through polymer membranes are especially attractive because environmental variations induce little if any error, and the total analytic process can be so designed as to accommodate the study of almost any and all gaseous hazards.

Although permeation-type monitors are the subject of this discussion, there are other passive systems that have merit for certain applications. Monitors based on effects response can be used where qualitative results are sufficient and low cost and convenience are important. Although quantitative sampling is not possible, relative concentrations are indicated by the degree of the induced effect. A second type of passive sampling is that based on the use of evacuated vessels. With such devices, a known volume of sample can be collected by simply opening the evacuated bottled or flask in the atmosphere under study to provide a grab sample. Such an approach can also be used for the collection of integrated samples over a predetermined time if the sample inlet is provided with a rate-controlling orifice. Evacuated vessels are limited as to the volume of sample that can be collected and therefore lack the necessary sensitivity for most work that is involved in personal monitoring.

Diffusion has been introduced as a convenient means of sampling. The diffusion technique was first introduced as a means of preparing standard gas atmospheres (1), and where conditions can be kept reasonably constant, such as in the laboratory, this approach has proven to be quite successful (2,3). For the preparation of standard gas mixtures, the liquid form of the reference material is allowed to diffuse into a dilute matrix system. The resultant conversion of a concentrated reference material to a dilute standard mixture can be reliable and convenient. The application of diffusion to the reverse problem--that is, the sampling of a dilute system with the quantitative collection of a minor constituent--has been advocated by the 3M Company and the Abcor Development Corporation, as well as by the British Defense Ministry at Porton Down. To date, the diffusion-type samplers have employed adsorption for the capture of the diffused sample. After the sample is collected, it is desorbed by suitable means and determined by conventional analytic processes such as gas chromatography. The badge is usually discarded after a single sample collection. In our experience, sample collection by means of diffusion is subject to some degree of error due to variations in humidity as well as by variations in the relative rates of movement of the collection device and the ambient atmosphere.

Permeation was introduced by O'Keeffe and Ortman (4) in 1966 as a means of preparing standard gas mixtures. This technique has been widely accepted as a method of choice for accurately introducing known amounts of sample gas into appropriate volumes of diluting atmospheres. The reverse of this process was introduced by Reiszner and West in 1973 (5) as a means for quantitatively collecting sulfur dioxide from ambient atmospheres. In this approach the ambient air was sampled by means of a simple cell containing a solution of tetrachloromercurate(II), stoppered at the top and enclosed on the bottom by means of a permeable membrane of a silicone polymer. The permeated SO_2 was absorbed and fixed as the sulfitodichloromercurate(II) complex which was subsequently analyzed by the well known West-Gaeke procedure (6). By prior determination of the calibration constant for a given membrane, the rate of permeation for SO_2 was determined; and, thus, the time-weighted average concentration for SO_2 for a known exposure could be established.

Permeation of a given gas through a given membrane is a function of the concentration of that gas. In general, permeation of a gas can be compared with dissolution. That is, a gas molecule coming in contact with a liquid dissolves and permeates into that liquid without the benefit of stirring. Instead of liquids, polymeric membranes can also serve as a permeation medium. Gas molecules coming into contact with such membranes dissolve and pass into the barrier until saturation is achieved. If a receiving system is introduced on the other side of the barrier, equilibrium is disturbed and the permeating molecules are removed, thus providing a means for quantitative mass transfer. Because of the fixed relationship between a given gas and a given membrane, the passage of a gas through membranes can be described by the equation:

$$k = \frac{Ct}{w}$$

where k = the permeation constant
C = concentration of the gas of interest, ppm
t = time of exposure
w = amount of gas absorbed, μg.

For use in personal monitoring, the above concepts can be applied, and knowing the permeation constant, or more properly, the calibration constant for an individual gas, sampling can be achieved and the concentrations of the gas of interest in unknown atmospheres for a given exposure period can be calculated,

$$C = \frac{wh}{t}$$

where C = the time-weighted average for the gas, ppm.

At this point it is proper to point out the difference between diffusion and permeation. Although there are similarities, there are subtle differences which may be significant in adjudging characteristics and, thus, applications. Unlike permeation, which is essentially a solution process as discussed above, diffusion represents the passage of molecules through holes in a discrete barrier where turbulence is minimized. Beyond the barrier, mass transfer across a stagnant space to a collecting surface provides a means for quantifying the transport process. The quantitative relationship is given by Fick's Law of Diffusion,

$$N = - DA\ (DC/DX)$$

where N = rate of diffusive transport, moles/sec
D = diffusivity of species, cm^2/sec
A = area of diffusion path, cm^2
C = concentration of species, moles/cm^3
X = path length, cm.

There are a number of general advantages to the permeation technique for sample collection. A unique advantage that has been disclosed over the past 8 years of laboratory and field experience is the almost indestructible nature of permeation-type devices. Since there is nothing to wear out or otherwise degrade, months or even years of service can be expected. Only the sorption medium needs to be replaced, and thus the cost for collecting any individual sample amounts to only a few cents. The long-term performance, together with the low cost of the original devices themselves, make this the lowest cost approach for reliable monitoring of gaseous pollutants. It is important to note also that the badge-type monitors are the ultimate in convenience and that they present no more hazard than the typical identification badge worn by plant personnel. This is in contrast to the impediment to motion and the danger of entanglement presented by the conventional battery, motor, pump, and tube personal monitors.

The versatility of the permeation approach for personal monitors provides a variety of options for the solution of different monitoring problems. Solid adsorbers such as silica gel and activated charcoal are of course well suited for use in the monitors. In addition, liquid systems are readily usable, as, for example, utilization of tetrachloromercurate(II) for SO_2 sampling and the use of solutions containing bromide and fluorescein for the simultaneous collection and determination of chlorine.

Permeation-type monitors have been widely field tested over the past 6 years, and in all cases excellent results have been obtained. Colleagues in the United Kingdom, Europe, Canada, and various parts of the United States have cooperated in the field tests, and their results have generally confirmed the results of the extensive testing that has gone into the original development of the individual monitor types.

Field use of any type of monitor emphasizes problems associated with environmental variations and stresses. The first problem faced in the development of permeation-type devices was that of temperature effects. The character of most polymeric membranes is very susceptible to changes in temperature, but silicone polymers were found to exhibit minimium variation over normal temperature ranges, and for some gases, such as vinyl chloride and chlorine, no errors were found over the range of 0° to 40° C. In general, therefore, temperature effects were found to be of little significance when the proper membrane was used. In general, the presence or absence of sunlight has been without effect, and humidity and relative air movement have been of no significance. The presence of a wide variety of copollutants in industrial atmospheres has presented no problems with any of the monitors developed so far.

The following discussion summarizes the essential make-up of five different devices that have been developed for the monitoring of sulfur dioxide, chlorine, alkyl lead, benzene, and vinyl chloride, respectively. In each case, the monitor itself is basically a hollow badge having a selected membrane enclosure and containing a sorption medium chosen especially for the collection and stabilization of the toxic gas of interest.

SULFUR DIOXIDE (5)
Membrane--dimethyl silicone, single backed
Sorber--sodium tetrachloromercurate(II), 1M
Analytic finish--conventional West-Gaeke spectrophotometric determination
Interferences--none
Temperature effect-- -0.5 percent ° C increase
Humidity effect--none
Relative air movement--no effect
Sensitivity for 8 hours exposure--0.01 ppm
Remarks--a catalytic stabilization can be used that permits sample collection over 1-to-4-week periods.

CHLORINE (7)
Membrane--dimethyl silicone, single backed
Sorber--buffered (pH 7) solution of fluorescein (0.005 to 0.0005 percent) and sodium bromide (0.31 percent)
Analytic finish--spectrophotometric or colorimetric measure of the color produced by the Cl_2-oxidation of bromide and resultant bromination of fluorescein to produce eosin
Interferences--none of significance
Temperature effect--none
Humidity effect--none
Relative air movement--no effect
Sensitivity for 8 hours exposure: 0.013 ppm
Remarks--sampling and simultaneous estimation of exposure results are possible by on-the-spot colorimetry.

ALKYL LEAD (8)
Membrane--dimethyl silicone, unbacked
Sorber--silica gel with desorption by means of ICl

Analytic finish--spectrophotometric measure of color produced with dithizone or an atomic absorption spectrophotometric determination

Interference--none; errors due to lead impurities in reagents minimized by use of silica gel rather than charcoal

Temperature effect-- -0.66 percent ° C for TEL and +0.81 percent per ° C for TML, thus essentially compensating for the usual plant mixtures

Humidity effect--none

Relative air movement--no effect

Sensitivity--0.2 µg, range 5 to 300 µg Pb/m^3

Remarks--analysis time only a fraction of that required in previous methods.

VINYL CHLORIDE (9)

Membrane--dimethyl silicone, single backed

Sorber--activated charcoal with desorption using CS_2

Analytic finish--gas chromatography

Interferences--none

Temperature effect--none

Humidity effect--none

Relative air movement--no effect

Sensitivity--0.02 ppm, range linear to at least 50 ppm

Remarks--widely field tested with excellent results.

BENZENE (10)

Membrane--silicone polycarbonate copolymer

Sorber--activated charcoal with desorption using CS_2

Analytic finish--gas chromatography

Interferences--none

Temperature effect-- -1.2 percent/° C

Humidity effect--none

Relative air movement--no effect

Sensitivity--0.02 ppm 8 hours, linear to at least 20 ppm

Remarks--analysis dependent on the purity of the CS_2 used for desorption.

SUMMARY AND CONCLUSIONS

Passive sampling of toxic gases for monitoring personal exposures can be accomplished reliably, conveniently, and at low cost by means of badge-type

TABLE 1
Results of Typical Field Tests

Sulfur Dioxide (area monitoring), $\mu g/m^3$

Permeation Device	Coulometric	West-Gaeke
<5	<25	<2
<5	<25	<2
156	144	
17	<25	
156		158
132		128
6		14
386		382

Vinyl Chloride, ppm

Permeation Device	Pump-Charcoal Tube
0.98	0.83
0.17	0.10
0.12; 0.11	0.07
0.05; 0.08	0.07
0.92; 0.97	0.88

Chlorine, ppm (preliminary data)

Permeation Device	Impinger
0.52; 0.67; 0.58	0.47[a]
1.10; 0.20; 1.15	1.10[a]
0.44; 0.49; 0.52	0.28[a]
2.70; 2.60	>0.40[b]
2.80; 2.10	>0.40[b]

[a] NIOSH methyl orange procedure

[b] Same as above using saturated solutions

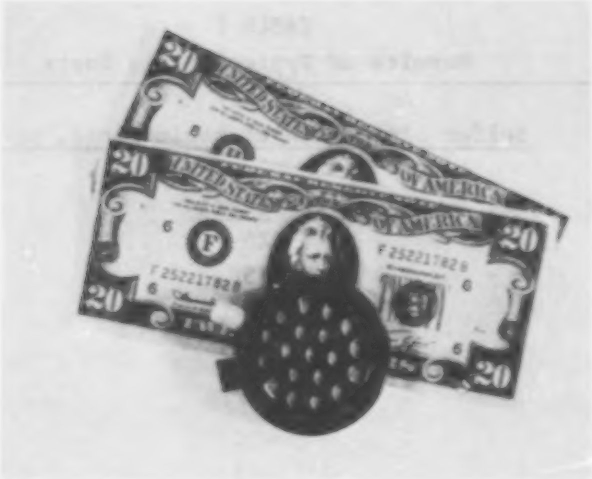

FIGURE 1. The MiniMonitor.

devices utilizing permeation for quantifying sample collection. Samples collected over periods of hours, weeks, or in some cases even months, are analyzed by conventional means to give the time-weighted average exposures.

Permeation-type monitors are indefinitely reusable because there are no moving parts to wear out, nor is there anything to degrade with time. The collected samples are adsorbed or absorbed by suitable means, removed after the sampling period, and analyzed. All that is required for repeated use of the monitor is to replace the sorber after each exposure; thus, these devices are the ultimate on the basis of convenience, cost, and reliability. The convenience is obvious because the monitors are single units having a size and weight comparable to that of an identification badge. The cost advantage is based on an initial cost of less than $80, which can be amortized over months or years of service--the only operational cost being a few cents for recharging with the appropriate sorber plus the cost of the subsequent analytical procedure. The reliability is attested to by extensive laboratory experience verified by widespread, independent, cooperative field studies (Table 1).

Permeation-type personal monitors, "The MiniMonitor" (see Figure 1), are available for a number of toxic gases with additional monitors currently under development. REAL, P.O. Box 3341, Baton Rouge, La. 70821.

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Discussion

SYKES: Dr. West, would you comment on the calibration procedures in these permeation-type adsorbers--specifically, on your system for calibrating?

WEST: We have standard gas atmospheres. So, we generate our standard atmospheres by diffusion for the alkyl lead, and for the rest of them I think we uniformly used permeation tube standards for generating our standard atmospheres.

We have a dynamic system in which the standard gas passes through the calibration device, which is something that we have published. If you look back at some of the publications you can see the details on that. We just simply insert or expose our monitors or our membranes to the dynamic standard gas atmosphere, and from that, determine the calibration constant.

MAGE: Dr. West, does any Government agency support your research right now?

WEST: Yes, I must give credit to the National Institutes of Health. We have had some support from them, and we have had some support from industry, and the university also supported it. Unfortunately, the support we have from NIH will be terminated in August. I am ready for any support you could give me, and I am open to any suggestions as to what you would like to have worked on.

BERLANDI: Dr. West, there has been a number of these gas badges at the conference that you have talked about. Are there any physical features of the badge that you have developed that allows it to volumetrically sample more air, or are all these badges essentially similar? Is the membrane somewhat unique in that it allows for more precision?

WEST: Incidentally, to impress some people, we can provide them with gold plating, so it will cost a little bit more if that is important.

At any rate, as far as the unique features of this particular badge go, yes, we have more capacity. If we are using adsorbents such as charcoal, we have somewhat more charcoal, and therefore greater capacity. There is no breakthrough, by the way, on these.

I certainly am not running down the other badges, but, the thing is is that these badges cost more than the 3M badge or the Gasbadge. These will run, say, anywhere from $40 to $80. But they are usable indefinitely. We have had one or two of these successfully performing, I guess, after more than 4 years. There is nothing to wear out, and since the sorber is poured out for the analysis and then replaced, that is the only cost after the initial cost of the badge. Then you pay a few pennies for whatever sorber you have to use in refilling it.

PETERS: Edward Peters, York Research. Perhaps I missed something earlier, but I notice that there is no effect from the movement of air.

WEST: That is right.

PETERS: The way I see it, the higher the movement of air, the more one might ingest these gases, and yet your instrument shows a constant level. Can you comment on that?

WEST: Well, what we are doing is that we are collecting the air at that particular spot and we are getting a time-weighted average of that particular exposure. Now, the rate at which the sample is collected here corresponds quite closely with the sample rate obtained, say, with a charcoal tube and pump. So, any variation that might be due to that would be, I think, characteristic of any sampling system.

SCHEIDE: I think the point to make is that you want those badges to be diffusion or permeation limited so that if the person is sitting still or walking down the hall, it should sample at the same rate. That, in effect, is what the membrane does.

Personal Air Pollution Monitors: New Developments

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With the advent of increasing awareness by the research community and the public at large of the potential short-term and long-term health hazards associated with airborne toxic contaminants, great emphasis has been placed on the development of new instrumental monitoring techniques to measure these hazards. In many cases, laws have been established to limit human exposures to various contaminants, regarding both occupational and ambient levels.

Historically, most ambient monitoring has been area monitoring, done with relatively sophisticated, expensive, and sensitive analytical devices that are hardly one step removed from the typical laboratory devices that require great care and attention in calibration and operation to obtain optimal performance. The use of this kind of analytical equipment for pollution monitoring in ambient air is dictated by the low concentration being measured.

In the occupational environment, quite different approaches have been undertaken. Typically, the toxic levels being measured are one to three orders of magnitude higher than permissible ambient levels, and, therefore, the choice of analytical technique, with adequate sensitivity, is greater. As additional toxicological and clinical evidence becomes available, there is a constant downward trend in permissible exposure levels of various contaminants. Typical examples of this process are vinyl chloride, acrylonitrile, and benzene. There is an ever-increasing body of data suggesting strongly that a very large percentage of the ambient and occupationally exposed population exhibits a multitude of subtle deleterious symptoms of exposure.

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Many instances are documented of the effects of very low levels of pollutants causing significant changes in behavior and hormone-enzyme balance that result in numerous symptoms that are difficult to treat because the industrial physicians involved are not aware of the causative agent.

The need to accurately define what an individual is actually exposed to, and to comply with OSHA requirements, has added impetus to develop personal monitoring systems for toxic substances. Oftentimes, standards are based on the limitation of sampling techniques, as well as toxicological data. For example, most OSHA exposure limits are time-weighted averages, based on averaging air concentration over a prolonged sampling period--i.e., 15 minutes, 2 hours, 4 hours, etc. Obviously, liquid impinger and charcoal tube techniques with typical sampling times, as suggested above, will have poor time resolution of changes in concentrations. The use of continuous, instantaneous readout monitors for substances (for which they are available), indicates that it is not unusual to see marked concentration flux over periods of 15 minutes or less in the occupational environment, as well as in ambient environments.

Since a short-term peak concentration may be as important as total dose in its effect on humans, it becomes important to define these exposures, where possible, and to provide immediate indication of concentration so that protective action can be taken to avoid excessive exposures. A number of passive monitoring techniques have recently been developed, including small, lightweight adsorption badges. Although these devices can be useful as diagnostic or screening agents, they cannot provide an exposure profile, and, most importantly, they only provide historical information--i.e., after it is too late to do anything about the exposure. To detect peak concentration requires, first, a sensing device small and lightweight enough to be readily worn by an individual in or near his or her breathing zone, with the capability of providing maximum time resolution and a continuous concentration output. A number of analytical techniques can meet these criteria, but not without limitations. Electrochemical cells and semiconductors are attractive techniques for personnel devices but oftentimes are limited by sensitivity and/or specificity problems. In these cases, the application often dictates success or failure of measurements relative to possible interferences.

One technique that offers great promise for further development and application is the detection of toxic gases using chemically impregnated paper tapes. In this case, contaminants which are collected on the tape react with the chemicals on the tape to produce a stain proportional to the mass concentrations of the contaminant. The strength of this technique is that not only can it provide time resolution (as short as 30 seconds), but also that the chemistry can be manipulated to obtain remarkable sensitivity (low ppb) and a high degree of specificity.

A personal sampling system using this detection principle (the MCM) has been commercially available for several years, and is capable of providing both a time versus concentration curve and total dose information for accurately defining personnel exposures. A modified MCM system, referred to as the Chromatox System, is currently in the final stages of development; it will expand even further the time resolution capabilities, as well as the overall versatility in utilizing new tape detection systems as they are developed from an ongoing research program. This system is analogous to hi-fi tape recorders, with the difference being that a chemical signal instead of an audio signal is recorded and played back.

To immediately increase the capabilities of the MCM and other personal detection devices that have a continuous output, a unique mircoprocessor profile alarm dosimeter (Chronotoximeter) has been developed. The Chronotoximeter is designed to accept an output signal from any detection system. The microprocessor takes a reading every second (this feature is adaptable to the sensor) and stores that datum in a temporary memory. At the end of 90 seconds, the data are processed and a 90-second average value is stored in a permanent memory. At the end of the exposure period, the Chronotoximeter is then interrogated to provide a time versus concentration curve and/or a digital printout of the stored data. The microprocessor can be programed to accept the input from other detection systems, in addition to the MCM. In fact, it has been designed with this intent so that a user would have maximum choice of detectors for data gathering. As detectors are changed, a "PROM" (programmable read only memory), calibrated to the detector calibration curve, is inserted into the Chronotoximeter, and the system is then totally compatible.

For ambient personal monitoring, the tape detection technique offers the greatest promise because of the ppb sensitivity and because of the infinite possibilities of chemical reactions to choose from to obtain appropriate specificity. An ongoing research program is continuing to develop new detection systems. The capability to begin meaningful surveys of general population exposures to compounds such as CO, NO_2, and SO_2 with the Chronotox System should provide a fruitful ground for research in the next several years.

The Chronotoximeter will also incorporate digital real time readout with high level and total dose alarm capability in one embodiment. This further enhances its usefulness, from a protection standpoint, to the individual wearing the device. Later phases of the development program will provide telemetry output of the Chronotoximeter so the data produced can be telemetered back to a central data center and appropriate warnings given to the wearer, when warranted. Such telemetry systems are already operational for measuring individual motion and heartbeat in hazardous occupational environments.

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Discussion

PETROVICK: Would you tell us what you are using and what the memory capacity of it is?

MILLER: Both answers at this point are proprietary.

PETROVICK: Another comment: I am pleased to see that someone is moving in that direction, because of the extrapolations from your hydrobodies to a true, physiological monitoring and and response type capacity. I commend you for that; I think that is the way to go.

MILLER: Just to comment in reference to what you say: I really didn't come here to talk about the physiological approach, but associated with this system, there is also a radio-operative system, and that radio-operative physiological system is one that an individual can wear, which will provide a heartbeat, that is tied into this complete system where you can radio the signal back to a central location.

So, if you have an individual out in an industrial environment--which would be a primary application here--where they may encounter an extremely high concentration of something that they cannot physically remove themselves from immediately, you will get an alarm signal as well as a direct heartbeat and respiration signal, sent back to a central control panel where individuals are continually monitoring, and then you can immediately take steps to send someone up. That system also now exists and is available, in conjunction with this.

PETROVICK: I would like to come back to that. That is very interesting, because if you pick up this week's US News and World Report, there is an article in there on cardiac heart attacks. It alludes to a 23 percent drop in fatalities from coronary attacks in the last 5 years with the implementation of some kinds of technology, particularly the emergency health care of the kind where help can get to the person within an hour. It is that crucial hour-long-period that I think you have. And if someone may have problems, even as simple as a bee sting, there are enzymes within the heart muscle that reside there that release themselves and partly are responsible for a coronary event. That is not my opinion--it is in the US News and World Report. I urge you to read it.

LIN: Will particulates be a strong interfering agent in the tape sampler?

MILLER: Generally speaking, we have found that not to be the case--actually, even in foundry operations where you have high ambient dust levels. And the reason is that the tape is continuously moving. It is not stopped on one spot. So primarily the stain that develops there is a function of the organics or whatever compound you are measuring and not of the particulates.

Also, most of the heavies drop out because of the relatively low flow rates that we are using, so you don't pick up a lot of the heavy particulates. Most of the submicron particles, because of the tape movement, don't create enough darkening of the tape system to make a significant difference.

Now, realistically speaking, that is not universally true, because I have found one or two situations where in fact the ambient dust level was so high that it did cause a significant background reading. In which case you had to correct for it by compensating your baseline. But that also, you know, can be done.

I might also add that in those situations the ambient dust level was so far above anything remotely approaching permissible exposures that it was a necessity, really, to correct the ambient dust levels before they worried about some of the other things they were sampling.

SHAW: What is the operating principle of this cell?

MILLER: I think it is best construed as an amperometric cell.

WEST: I believe you mentioned you have gotten away from the lead acetate. What do you use?

MILLER: I will tell you that we do use lead acetate. However, a little modern chemistry and engineering has, let's say, taken the basic lead acetate and made it workable, in effect, in a real-world environment.

There are units available that use the old lead acetate that require all kinds of unbelievably complex humidification schemes. Our system does not require that. Again, it is proprietary, but suffice it to say that we build the water into the tape.

WEST: We'll take your word for that, because that is important.

MILLER: That is critical. The sensitivity is tremendous, but it has always been the humidity effects that have really been the problem one has to cope with.

A New Sampling Tool for Monitoring Exposures to Toxic Gases and Vapors

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INTRODUCTION

Air sampling devices are needed to provide a variety of exposure information, including:

1) Occupational exposure information concerning employees in a plant and environmental exposure information of the population in an area surrounding a given plant.

2) Personal and fixed-station (area) exposure information.

3) Information concerning immediate (acute) versus long-term (chronic) health hazards.

4) Peak versus time-weighted average exposure data (or episode versus average concentrations).

5) Continuous versus integrated sample measurements.

These various applications require a number of different sampling devices, each having certain advantages and limitations. A comprehensive summary of the uses of air quality monitors in measuring the exposure of the general public to air pollution is explored by Lance Wallace in Reference 1.

The purpose of this paper is to discuss a passive sampling device, the

GASBADGE™[*] dosimeter, and its applications to date (primarily in occupational health monitoring), and to suggest which of the exposure information needs presented above it can best satisfy.

THE GASBADGE ORGANIC VAPOR DOSIMETER

The GASBADGE organic vapor dosimeter is a 1 and 1/2-ounce sampling device which can easily be worn by an individual to collect time-weighted average exposures to organic vapors. Since it requires no air sampling pump, it is often referred to as a "passive" sampler. The GASBADGE dosimeter is analogous to and as convenient to wear as the radiation film badge.

The dosimeter (Figure 1) contains an activated carbon collection element which is removed after exposure for subsequent analysis. To determine the time-weighted average exposure, the element is removed from the dosimeter and placed in a sealed vial. The organic material collected on the element is then desorbed using carbon disulfide or another appropriate solvent and analyzed by gas chromatography. The dosimeter is reusable and can be easily reloaded with a new collection element. Additional elements (other than charcoal) can be used to collect other gases and vapors.

The components of the dosimeter (Figure 2) include (from bottom to top):

1) A sliding cover to prevent contamination, or exposure, for short periods of time.

2) A dosimeter front with a carefully defined opening to allow diffusion of gas or vapors into the dosimeter.

3) A draft shield made from a nonreactive porous material.

4) An open grid to define the diffusion geometry and minimize internal mixing.

5) A replaceable collection element.

6) A caseback with a spring clip for attachment to the individual.

OPERATING PRINCIPLES

Generally, the first reaction to the GASBADGE dosimeter centers around

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[*] GASBADGE is a trademark and registered servicemark of Abcor Development Corporation, Wilmington, Mass.

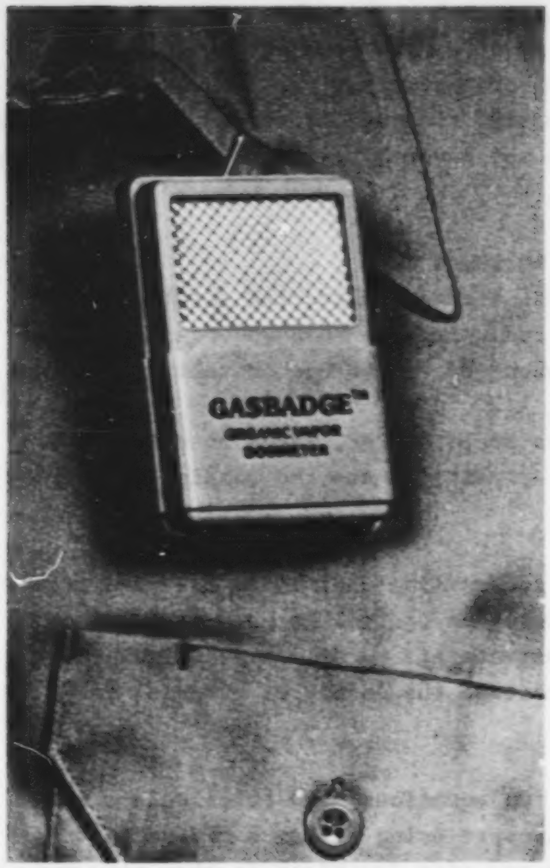
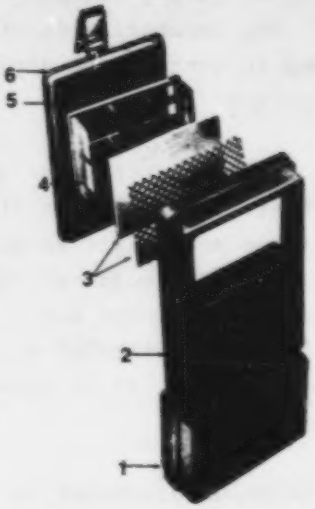


FIGURE 1. The GASBADGE Organic Vapor Dosimeter.

COMPONENTS



1. Sliding protective cover prevents contamination or exposure for short periods of time
2. Badge front with opening allows diffusion of gas or vapors into dosimeter
3. Draft shield made from nonreactive porous material
4. Open grid defines diffusion geometry, minimizes internal mixing
5. Replaceable collection element
6. Dosimeter back with spring clip

SPECIFICATIONS

Dimensions:	2 x 2 9/16 x 5/8 in. (5.1 x 6.5 x 1.6 cm)
Weight:	1.5 oz. (43g)
Power:	None
Collection Element:	Activated carbon
Analysis Method:	NIOSH P&CAM 127 (modified)
Sampling Time:	8 hr nominal
Sampling Range:	0.2-160 ppm/8-hr TWA (benzene)
Accuracy:	± 25%
Shelf Life:	2 years
Air Velocity:	15 fpm (0.08 m/s) minimum. Normal industrial plant air velocity exceeds 20 fpm (0.1 m/s)
Patent:	U.S. Patent 3,985,017

FIGURE 2 (right). GASBADGE components and specifications.

the absence of an air sampling pump. The reaction is either positive or negative. The positive reaction is: "Now I won't have to spend all my time calibrating my pumps, charging batteries, or just trying to keep the pumps running." The negative side of the "no pump" response is this: "If it doesn't have a pump to control the air flow into the device, how will I know the volume of air sampled?"

What these two responses point out is that:

1) There is a fundamental difference between collecting samples using sampling tubes and an air sampling pump and using the GASBADGE dosimeter because the GASBADGE dosimeter does not depend on the volume concept associated with air sampling pumps; and

2) Since the GASBADGE dosimeter has no rotometer, makes no noise, and has no moving parts, it is impossible to physically see the sample collection in process.

The GASBADGE dosimeter is based on controlling the random but predictable molecular movement of gas molecules rather than controlling air flow. What Abcor has done with the organic vapor dosimeter is to utilize physical chemistry principles of vapor diffusion to control the amount of material collected by the collection element.

Figure 3 shows a comparison of the two equations used to calculate the ppm concentration of an organic vapor exposure using either a diffusion dosimeter or a pump sampler. Both equations are time dependent in that more material will be collected for longer exposures at a given concentration (up to the capacity of the device).

The first two parts of each equation are basically the same. The difference between the two equations is in Section III, or what is labeled the "Transport Force." In Section III, the flow-rate or volume component of the pump sampler equation is replaced by three physical constants which control the mass of material collected by a diffusion-based sampler, namely:

1) The length of the diffusion path;

2) The cross-sectional area onto which the gas or vapor is diffusing;

3) The diffusion rate of the gas or vapor in air, determined by experimental methods.

To accurately determine measurements of employee exposures using a charcoal tube sample collected with an air sampling pump, the flow rate must be precisely controlled at a known constant level throughout the sampling period.

I Measurement of Collected Sample	II Standard Conditions and Molar Conversions	III Transport Force
Diffusion Dosimeters		
$ppm = \frac{(\mu g_{sample} - \mu g_{blank})}{\text{desorption efficiency}}$	$\times \frac{1}{mw} \times 22{,}400\ cc/mole \times \frac{T^{o}\ K}{273^{o}\ K} \times \frac{760\ mmHg}{P\ mmHg}$	$\times \frac{\lambda_{(cm)}}{D\left(\frac{cm^2}{sec}\right) A_{(cm^2)}\ t_{(sec)}}$
Pumped Sampler		
$ppm = \frac{(\mu g_{sample} - \mu g_{blank})}{\text{desorption efficiency}}$	$\times \frac{1}{mw} \times 22.4\ \ell/mole \times \frac{T^{o}\ K}{273^{o}\ K} \times \frac{760\ mmHg}{P\ mmHg}$	$\times \frac{1}{\text{Flow Rate}_{(\ell/min)} \times T_{(min)}}$

λ = Diffusion Length (cm)
D = Diffusion Coefficient (cm^2/sec)
A = Cross-sectional Area (cm^2)

FIGURE 3. Diffusion and air sampling pump equations.

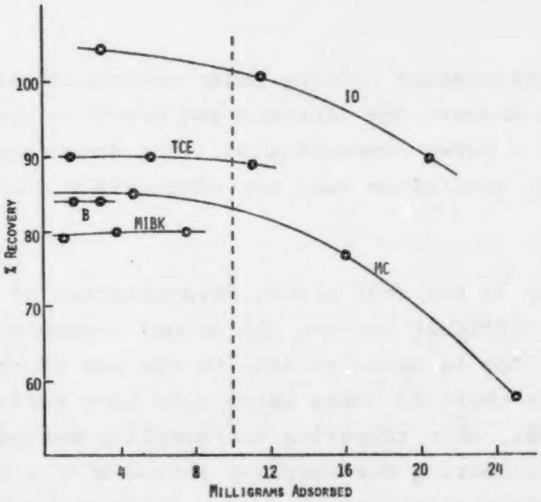


FIGURE 4. Percent recovery versus milligrams adsorbed. (Source: Mazur, J.F. et al. A New Personal Sampler for Organic Vapors. Paper presented at the AIHA conference, May 1977.)

If the flow rate changes during sampling, or it is not verified before and after sampling, the calculated results will be in error.

Passive samplers, operating on the diffusion principles, are dependent not on flow but on careful definition of the physical dimension of the sampling device and on making certain that the only force causing the collector to operate is gaseous diffusion. The GASBADGE dosimeter does this by creating a dead air space that is relatively unaffected by changes in air velocity between the draft shield and the collection element. The GASBADGE dosimeter works, in effect, because the draft shield prevents air flow into the device, thereby ensuring that the amount of gas or vapor collected is determined only on the diffusion rate (molecular movement) of gas or vapor in the air being monitored.

PERFORMANCE TEST RESULTS

Two types of performance testing are:

1) Testing under carefully controlled laboratory conditions with a known concentration and environment.

2) Testing primarily in industrial (occupational) environments under field conditions which present more variability and essentially unknown concentrations.

The advantage of performance testing under controlled laboratory conditions is that one can measure the accuracy and precision of the sampling method when compared to a known concentration. The disadvantage is that testing under laboratory conditions does not necessarily duplicate the real world.

While field testing is the real world, determination of accuracy and precision is much more difficult because the actual concentration is generally unknown and varying and can be measured only by the use of other secondary sampling devices such as charcoal tubes which also have variations in their accuracy. In other words, when comparing two sampling methods under field conditions, one may be comparing one sampling method with a potential error of plus or minus 25 percent with another device which has a similar error range. This means one could expect variations between the results of two such sampling methods of as much as plus or minus 50 percent.

For these reasons, Abcor has relied on controlled exposure testing by Abcor and other groups to determine the accuracy of the GASBADGE dosimeter for various organic materials. Correlations between side-by-side field samples collected using organic vapor dosimeters and other suitable sampling methods verify that there is general agreement between two (or more) sampling methods under varying field conditions.

The U.S. Army Environmental Hygiene Agency (USAEHA) conducted an extensive evaluation of this monitoring device (2). Table 1 shows the percent recovery and relative concentration obtained by the USAEHA for seven different organic compounds. The compounds tested represent seven different classes of organics; namely, an aromatic, an alkane, an alcohol, a ketone, an ester, a halogenated alkane, and a halogenated alkene. The compounds were individually sampled to determine percent recoveries for each in the 1/4, 1, and 2x the TLV concentration range, and to determine if the dosimeter compared favorably with the recoveries previously obtained by the USAEHA for charcoal tubes. Since the dosimeter data were so reproducible, the U.S. Army Environmental Hygiene Agency felt that the results could easily be corrected for the slightly lower percent recovery levels for absorption/desorption efficiencies, just as charcoal tube data are corrected.

Figure 4, again from the USAEHA study, shows a plot of percent recovery versus total mg adsorbed for iso-octane, trichloroethylene, methyl chloroform, n-butanol, and MIBK. The results of this experiment indicated that the percent recovery was relatively independent of ambient concentration when less than 10 mg of material is loaded on the collection element. For this reason, Abcor recommends that the maximum loading of GASBADGE collection elements not exceed 10 mg total solvent.

Many customers have asked if the GASBADGE dosimeter measures mixtures as well as single-component vapors. The data in Table 2, again from the USAEHA study, show that diffusion operates effectively for mixtures of organic compounds as well as when the compounds are each monitored separately. This holds true as long as the mixture does not exceed the maximum recommended loading of 10 mg total solvent.

Tables 3 and 4 show the accuracy and precision of the GASBADGE dosimeter for benzene and acrylonitrile monitoring. Table 3 was compiled from performance testing conducted by Abcor for benzene exposures varying from 0.28 ppm to 4.69 ppm. It shows the mean dosimeter concentrations, systematic error, and relative standard deviation for the GASBADGE organic vapor dosimeter at various levels. The pooled values of the individual test levels are a measure of the overall accuracy of the device for all exposure runs combined and in-

TABLE 1

Percent Recovery Versus Relative Concentration

COMPOUND	AMBIENT CONC. (PPM)	TOTAL MG ADSORBED	AVERAGE % RECOVERY	CHARCOAL TUBE
Benzene	2.5	0.076(a), (b)	76	
	10.0	0.37	94 ± 4	97
	20.0	0.71	89 ± 4	
Iso-Octane	75	3.0	104 ± 3	
	300	11.5	101 ± 3	NA
	600	20.5(c)	90	
n-Butanol	12.5	0.28	64	
	50.0	1.5	84 ± 3	88 ± 5‡
	100.0	2.9	84 ± 5	
MIBK	25	1.0	79 ± 4	
	100	3.8	80 ± 6	93
	200	7.5	80 ± 2	
n-Butyl Acetate	37.5	1.5	93 ± 3	
	150.0	5.8	88 ± 4	95‡
	300.0	10.5	84 ± 4	
Methyl Chloroform	87.5	4.7	85 ± 2	
	350.0	15.8(c)	77 ± 3	100
	700.0	25.5(c)	58	
Trichloro-ethylene	25	1.4	90 ± 2	
	100	5.7	90 ± 3	95
	200	11.1	89 ± 3	

(a) Too low for accurate quantitation.

(b) Percent recovery improved by Abcor to 94 percent by modifying the analytical technique used in the USAEHA study.

(c) Overload conditions.

‡ From the literature.

Source: Mazur, J.F. et al. A New Personal Sampler for Organic Vapors. Paper presented at the AIHA conference, May 1977.

TABLE 2

Percent Recoveries for a Four-Component Mixture

COMPONENTS	AMBIENT CONC. (PPM)	% RECOVERY	REFERENCE % RECOVERIES*
Iso-Octane	46.1	102	101-104
Benzene	80.0	86	89-94
MIBK	56.6	75	79-80
Butyl Acetate	54.0	90	84-93

*Percent recovery in the absence of other components

Source: Mazur, J.F. et al. A New Personal Sampler for Organic Vapors. Paper presented at the AIHA conference, May 1977.

dicate that the GASBADGE dosimeter is within plus or minus 20 percent at a 95 percent confidence level.

Similar accuracy for the GASBADGE dosimeter is demonstrated in Table 4, which summarizes data collected by Dow Badische (3) for monitoring exposures to known concentrations of acrylonitrile. After conducting laboratory measurements to determine the accuracy of the GASBADGE dosimeter, Dow Badische performed field tests on a side-by-side basis with charcoal tube samples. The data from the field testing demonstrated that the GASBADGE organic vapor dosimeter is comparable to the charcoal tube technique.

CURRENT APPLICATIONS OF PASSIVE SAMPLERS FOR PERSONAL EXPOSURE MONITORING

The major uses of the GASBADGE organic vapor dosimeter have centered around potential occupational exposures, including:

1) Monitoring employee exposures to benzene in petroleum refineries, benzene manufacturing facilities, pharmaceutical companies, laboratories, and other similar industries.

2) Monitoring exposures of field personnel to benzene in remote petroleum pipeline and pumping station locations where the dosimeters are dis-

TABLE 3

GASBADGE™ Organic Vapor Dosimeter Performance Data

Benzene Monitoring

(8-Hour TWA Exposures)

Exposure Concentration (ppm)	Number of Dosimeters	Mean Dosimeter Concentration	Standard Deviation (ppm)	Systematic Error	Relative Standard Deviation (RSD)	Error Range to a Confidence Level of 95% Based on Systematic Error ±RSD
0.28 ppm	4	0.25 ppm	0.01 ppm	-11%	4.0%	-19.0% to - 3.0%
0.5 ppm	5	0.56 ppm	0.01 ppm	+12%	1.7%	+ 8.6% to +15.4%
0.5 ppm	5	0.49 ppm	0.01 ppm	- 2%	2.0%	- 6.0% to + 2.0%
0.56 ppm	9	0.64 ppm	0.03 ppm	+14%	4.7%	+ 4.6% to +23.4%
0.56 ppm	10	0.60 ppm	0.04 ppm	+ 7%	6.7%	- 6.4% to +20.4%
0.97 ppm	20	0.98 ppm	0.04 ppm	+ 1.0%	4.1%	- 7.2% to + 9.2%
1.90 ppm	15	2.24 ppm	0.10 ppm	+17.9%	4.5%	+ 8.9% to +26.9%
4.69 ppm	20	5.25 ppm	0.30 ppm	+11.9%	5.7%	+ 0.5% to +23.3%
Pooled Values				+ 8.5%*	4.8%**	- 1.1% to +18.1%

$$\text{Systematic Error} = \frac{\text{Mean Dosimeter Concentration} - \text{Exposure Concentration}}{\text{Exposure Concentration}}$$

$$\text{Relative Standard Deviation} = \frac{\text{Standard Deviation}}{\text{Mean Dosimeter Concentration}}$$

*Calculated using a weighted systematic error.

**Calculated using the technique specified by NIOSH for evaluating the accuracy of methods for the standards completion program, Summary of Statistical Terms and Formulas, S112-D1 (Attachment D). The mathematical equation is expressed as:

$$\overline{RSD} = \sqrt{\frac{\sum_{i=1}^{n} f_i \,(RSD_i)^2}{f}}$$

where:

$\overline{RSD}$ = Pooled Relative Standard Deviations (Coefficient of Variation)

f_i = degrees of freedom, equal to number of observations minus one, at the i^{th} level

RSD_i = Relative Standard Deviation of the observations at the i^{th} level

$f = \sum_{i=1}^{n} f_i$

TABLE 4

GASBADGE™ Organic Vapor Dosimeter Performance Data
Acrylonitrile Monitoring

Exposure Concentration	Number of Dosimeters	Mean Dosimeter Concentration	Standard Deviation	Systematic Error	Relative Standard Deviation (RSD)	Error Range to a Confidence Level of 95% Based on Systematic Error ±2 RSD
0.74 ppm	10	0.75 ppm	0.03 ppm	+1.4%	4.0%	- 6.6% to + 9.4%
8.9 ppm	16	8.67 ppm	0.83 ppm	-2.6%	9.6%	-21.8% to +16.6%
19 ppm	7	19.14 ppm	2.41 ppm	-0.7%	12.6%	-25.9% to +24.5%
		Pooled Values		-1.0%*	9.1%**	-19.2% to +17.2%

This data demonstrates that the GASBADGE organic vapor dosimeter meets the accuracy requirements of the Temporary Emergency Standard for Acrylonitrile issued by OSHA on January 17, 1978.

The above data is a summary of results of a study conducted by the Dow Badische Company, exposing the dosimeters in a dynamic test chamber for 6-8 hours. As a further check, eighteen GASBADGE dosimeters were worn, side-by-side with charcoal tube samples under field conditions. The data from both the dynamic testing and field testing show the GASBADGE technique is accurate, reproducible and comparable to the charcoal tube technique. A copy of the complete test data is available from Abcor Development Corporation or W. O. Calhoun, Quality Control Laboratory, Dow Badische Company, Post Office Drawer D, Williamsburg, Virginia 23185.

$$\text{Systematic Error} = \frac{\text{Mean Dosimeter Concentration} - \text{Exposure Concentration}}{\text{Exposure Concentration}}$$

$$\text{Relative Standard Deviation} = \frac{\text{Standard Deviation}}{\text{Mean Dosimeter Concentration}}$$

*Calculated using a weighted systematic error.

**Calculated using the technique specified by NIOSH for evaluating the accuracy of methods for the standards completion program, Summary of Statistical Terms and Formulas, S112-D1 (Attachment D). The mathematical equation is expressed as:

$$\overline{RSD} = \sqrt{\frac{\sum_{i=1}^{n} f_i \, (RSD_i)^2}{f}}$$

where:

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RSD_i = Relative Standard Deviation of the observations at the i^{th} level

$f = \sum_{i=1}^{n} f_i$

tributed to the field, reloaded in the field, and samples sent in vials to central laboratories for analysis.

3) Monitoring employee exposures to various chlorinated solvents used in metal degreasing and other cleaning operations, such as trichloroethylene.

4) Monitoring employee exposures to acrylonitrile from the manufacturing of the basic material through its use in ABS injection molding operations.

In addition to its use in a traditional industrial hygiene sampling program of a large plant under the supervision of an industrial hygienist, the GASBADGE dosimeter lends itself to "self-administered" sampling of personnel at remote locations or in plants where there is no industrial hygienist. The GASBADGE dosimeter makes sampling easier and even possible in areas where air sampling pumps cannot practically be sent or used due to the lack of trained personnel.

Additional areas in which the GASBADGE dosimeter has or will be used include:

1) Evaluations of hospital personnel having exposure to various anesthetic gases and other gases and vapors.

2) A study of vocational education students to determine qualitative exposure information for a variety of organic vapors found in painting and decorating, plastic technology, and auto body shops.

3) An evaluation of the exposures of individuals to various dry cleaning solvents

4) A study of the exposure of college art students to various solvent vapors present in silk screening operations.

POTENTIAL APPLICATIONS OF PASSIVE SAMPLERS FOR MONITORING COMMUNITY EXPOSURES

The GASBADGE dosimeter provides a sampling device which can be used to obtain personal exposure information related to health effect studies for environmental as well as occupational exposures.

The primary purpose of this sampling device is for personal monitoring, although it could be used to obtain area monitoring information. Since it is not direct reading and has no alarm to warn of overexposure, it should be used for monitoring chronic rather than acute health hazards. While it is effective for short-term monitoring (1 hour or less), it should normally be used for obtaining time-weighted exposure information over several hours. It should be used for obtaining integrated sample measurements rather than as a continuous monitor to measure changes in concentrations.

Since the GASBADGE dosimeter does not require an expensive air sampling pump nor the calibration and training requirements associated with pumps, it can be distributed and collected in a number of ways (mail, a central distribution point, or by personal visit). In other words, it is both economical and relatively easy to use in a large-scale population study.

Performance data indicate the success of passive samplers for monitoring occupational exposures to a variety of gases and vapors. It would be appropriate and necessary to conduct similar performance tests to determine the effectiveness of the GASBADGE dosimeter for monitoring exposures over days or weeks (rather than 8 hours) at levels in the parts-per-billion rather than the parts-per-million sampling range. We believe such testing will demonstrate that this sampling approach has the ability to provide valuable exposure information for a variety of population groups in the home and outside environment as well as in the workplace.

REFERENCES

1. Wallace, L. Personal Air Quality Monitors: Past Uses and Present Prospects. Paper presented at the 4th Joint Conference on Sensing of Environmental Pollutants, American Chemical Society, 1978.

2. Mazur, J.F. et al. A New Personal Sampler for Organic Vapors. Paper presented at the American Industrial Hygiene Conference, New Orleans, La., May 1977.

3. Calhoun, W.O., Silverstein, L G. Personal Monitoring for Acrylonitrile Using the Abcor GASBADGE™. Dow Badische Company, Williamsburg, Va., September 1977.

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Panel Discussion

Panel members for the following discussion were: Dr. David Mage, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency (EPA); Dr. Lance Wallace, Office of Monitoring and Technical Support, EPA; Mr. Otto White, Brookhaven National Laboratories; Mr. Mathew Petrovick, Health Effects Research Laboratory, EPA; and Dr. Manny Shaw, Interscan Corporation.

MAGE: Thank you very much for returning this afternoon. We are going to try to summarize for the benefit of the record, as well as for the discussants, our impressions and conclusions of what we have learned, and the directions that we feel we should be going in.

You will have an opportunity to make remarks for the record after the panel members have given their summary.

I am going to start off by recognizing the panel members--Dr. Lance Wallace, Mr. Otto White, Mr. Matt Petrovick, Dr. Manny Shaw, and finally, myself.

WALLACE: I don't have any prepared remarks. I am still trying to come to grips with everything that I have learned the last few days, which has been a large amount of information to try to take in.

Frankly, my horizons have been broadened. I came into this conference thinking of personal monitors basically on the physical-chemical side of it

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and of making that type of measurement. I now see that the advances in the methods of measuring physiological responses are great enough that they have opened up to us a possibility of dose response measurements that I hadn't really envisioned before.

The microcomputer aspects, that would enable us to take these continuous measurements of both dose and response and provide complete 8-hour or 24-hour readout, appear to be extremely promising for the future.

So, these three aspects--the physical-chemical side, the physiological side, and the microcomputer side--appear to be very promising.

Among the monitors that are available now, I see several obvious representatives: one is the electrochemical family for CO for which we already have the ESI instrument, the GE instrument, and we have a promise from our industry representative of an Interscan instrument in the next year or so.

For NO_2, the Palmes effort has been field tested and is getting indoor levels in the 50 parts-per-million range near gas stoves.

In another area, the organics area, it is clear that we have several specific monitors. Dr. West has benzene, toluene, alkyl lead, vinyl chloride, and halogenated hydrocarbons. These monitors have been used in both the workplace and home environments.

Both Minnesota Mining and Manufacturing (3M) and Abcor have special activated charcoal elements that can adsorb any organic materials that can't be absorbed on activated carbon. Those dosimeters are available right now so that we can monitor out in the field. That is what they have been doing--monitoring a wide range of organics.

Each badge is not specific for a particular organic. You can use one badge and monitor a wide variety of them. You just break it down in the analysis. So, those are available now for workplace monitoring.

These badges have not been tested at the parts-per-million levels found in ambient air, since there has been no need to do so up to this time.

I have the feeling at the moment that we do not have available personal monitors for ozone, although we did see the Mast instrument, which is a portable one.

In regard to fine particulates, the Harvard group does have a set of instruments that they have adapted themselves. I am not certain whether we can call these instruments working personal monitors or not, because they are rather bulky. In their study that they described previously, one third of the persons in the first sample group who tried it gave it up on the first day. Apparently, more work is needed here.

In regard to SO_2, it is no problem at all. Dr. Philip West has been doing that for some time, not really as a personal monitor, but for workplace and ambient area monitoring in general. Personal monitoring can be done with the permeation approach, and it can be done over long periods of time. Stability is ensured by converting the SO_2 to sulfuric acid, and the analysis proceeds from there. This provides a completely stable system. These badges can be used for levels of 0.01 ppm and below.

The one remaining thing that I would like to mention is the prospects for the future in the development of personal monitors. It appears from what we have heard in the last 2 or 3 days that the most emphasis and the largest payoff in the future may be the area of fine or respirable particulates. We have a great interest in that within EPA. A particulate dosimeter presents a possibility of collecting the material and then subjecting it to analysis for a spectrum of individual pollutants. And the other main aspect would be the organic monitors that we heard about from Dr. Joseph Brooks, Leah Daniel, Dr. Phil West, and other people here. We may be able to do classes of organics. We may be able to do individual organics of interest. Monsanto staff are going to check 20 carcinogens. They have a 3-year program of which they have completed the first year. This may be an area in which we can expect great advances in the future.

MAGE: Thank you very much, Dr. Wallace.

WHITE: Certainly, this week has been enlightening to me, and hopefully the information from this meeting will help formalize the final report that my committee is working on. Certainly we are aware of pollution conditions that exist, not only in the occupational environment, but also in the general environment, that resulted in the conditions of black lung, the Donora, Pa., episode, and the London air pollution situation.

One does not have to ponder long in thinking in terms of why we need to monitor from the epidemiological standpoint or the compliance standpoint. We need to determine whether or not the workplace or the environment is indeed safe. These represent challenging areas for not only the industrial hygienist, but also for the environmentalist--that is, to develop the instrumentation to perform that monitoring.

As I see it, we are still on the threshold of trying to develop instrumentation for some of the more common pollutants such as CO and oxides of nitrogen. We have yet to begin tackling what may indeed be the more difficult components of the environment. We can look at the incidence of cancer per county as published by HEW.

It has been reported in the literature that a high percentage of cancers are environmentally or anthropogenically induced. This represents a more challenging area of monitoring than our traditional oxidants, NO's, CO's, total particulates, and hydrocarbons.

So, I think yes, there is a need for defining where the instrumentation development should come from and what should be analyzed. I think there has been a lot of discussion in terms of the physical-chemical aspects of monitoring. There has been some discussion about monitoring the physiological stress on the individual.

I personally am concerned about long-term effects, as to whether or not that kind of data per individual would allow us to explain some of the long-term effects. Maybe it is going to be necessary to perform these exposure monitoring activities for a long period of time. I guess I am just not informed as to what health effects you are going to be looking for over a short term for some of the ambient ranges of pollutants.

But I also think we should probably search the horizon for the types of tools that we are looking for. Almost no comment has been made on some of the biological systems, bioassay systems. I recall about 12 years ago when I was here at the University of North Carolina, and we were looking for bioindicators for oxidant and ozone, using white pine seedlings.

Although the Ames test was not intended to be a bioindicator, I certainly think it represents an area where research and development may be warranted in terms of defining whether or not that tool can be used as an indicator. That may be of particular interest for some of these organics where there is a potential of there being a large host of compounds. Some decision is going to have to be made as to which compounds represent types of interest.

Maybe what is significant is a measurement of biological activity of the atmosphere as opposed to measurement of benzopyrenes and benzene soluble fraction.

There are a lot of biological screening tests. At Brookhaven we have been using tradescantia, which is a plant system. Our tradescantia has been cloned to be very sensitive to chemical mutagens. It has been used in a test system trailer which has been going around the country with an EPA air pollution monitoring system. That is an area where there may be some development in terms of a personal monitor.

I know that you can take the buds from the tradescantia system and wear it on the lapel. As a proposal, maybe this is something--maybe we could devise a corsage or something that could be worn on an individual's lapel and after a week of use and with some hydroponic solution to keep this system wet and moist, you would be able to score this. I think this is a very easy system to score by continuing visible mutations. This may indeed give you an indication of the biological activity of the atmosphere.

I think that in terms of my own concerns for identifying those kinds of pollutants that are of interest for the coal conversion and oil shale industries, we are looking at the occupational environment now. Unless these systems are quite tight and enclosed, the emissions may be your CO and oxides of nitrogen of the future. The commercialization and applications of these systems are expected to come on line within the next 4 or 5 years, and they thus represent a concern to us all.

The monitoring technology is there. We are in trouble in terms of defining what to measure and in terms of identifying health effects. If we are going to try to eliminate Workmen's Compensation claims that are comparable to the claims for black lung, which have been reported to be $1 billion annually, then we are behind in our efforts to develop the technology.

In regard to the comments made by the developers and manufacturers of these personal monitors, one question that came up repeatedly is, "Where is the market?" I think that as pollutant standards are developed, in terms of defining what is a safe environment and the frequency and the type of precision that is required in order to ensure that environment, that at least in the occupational environment the instrumentation need is going to be quite high.

So, I think that there is that particular market area. There is a mandate to make sure that instrumentation is simple, uncumbersome for the individual to wear, and cheap. If you are talking about sampling some representative fraction of the work force, you can't afford to stay in business and buy $5,000, high technology devices to monitor a representative component of that work force. But you are going to have to have simple, lightweight devices. That is where I think the passive dosimeters are needed.

I think, however, that there are other areas where you need more information than passive dosimeters can provide, such as special survey devices for high hazards and potentially acute exposures.

And there are areas where area monitors are appropriate. If the workplace conditions are fairly stable and you are protected, say, from micrometerological episodic conditions, area monitors can provide the type of monitoring that is required.

This particular meeting has been enlightening for me. It has provided me with an insight in terms of the fact that not only in the occupational environment, but also in the ambient environment, are there instrumentation needs.

I think there should be a unified effort addressed to the suppliers so that what technology is developed is useful to all sectors.

MAGE: Thank you very much, Otto. Our next speaker is Matt Petrovick, from EPA's Health Effects Research Laboratory.

PETROVICK: I would like to reflect a little on my impression of this conference. I think I agree with the other panelists in that it has been quite an enlightening and an exciting educational experience.

I see a number of opportunities in so many areas that we are not going to be able to talk about them all. But I would just like to reflect on a few.

Specifically, in this morning's initial session, Dr. Mage mentioned a wide variety of the types of sensors that we are going to look at. He touched on the topic of agricultural pesticides. Perhaps I might have missed a few sessions, but I didn't hear too much other comment in that direction. Maybe I have a lot to learn on the sensors that are used in this area.

However, I would like to identify for this group an area where the badge-type membrane devices and sensors that I have heard about here today can be very effectively applied in terms of manufacturers' motivation, health effects monitoring, and dosimeter measuring. And that is specifically in the area of agricultural spraying; that is, agricultural spraying with aircraft. If I can just briefly give you some background information on this. The Federal Aviation Administration (FAA) happens to be in a great state of alarm at the present time due to the increased incidence of agricultural aircraft accidents.

Not only are the pilots having problems in the flying of these aircraft, but the manpower that happens to be coordinating with these people have problems. The farmer's wife standing at the end of a row that is to be sprayed, a coworker filling the spray tanks of the plane, and the field workers are all exposed to the atomized droplets by direct skin contact. When the pilot finishes a summer of spraying, he might have acquired a significant build-up of these pesticides, without being aware of it. It is suspected by the FAA that the pilots' perceptive and cognitive judgments may suffer. For example, there could be central nervous system disorders which have to do with motor reaction, sensory perception of the visual tract, and judgment. It is that particular aspect that the FAA feels might be responsible for the pilot losing control of the aircraft and going in. That is only one aspect.

The other aspect is that there is not enough attention being given to the person on the ground who is getting belted with a lot more pesticide than the pilot. Over a summer of this kind of activity, there is widespread opportunity to look at a population that is exposed and isn't being monitored very well.

On the other side of the coin, from the research standpoint and from the clinical epidemiological standpoint, EPA has invested a large sum of money into design and development of a clinical-environmental laboratory here in Chapel Hill--a clean air facility and a controlled atmosphere facility. It just seems illogical that we can't transpose some form of clinical protocol out of a laboratory of this kind and, in this specific instance, into a small, single-cockpit laboratory where that pilot is sitting. These are air conditioned cockpits which leak like a sieve. The air conditioning flows back through, picks up the pesticide, passes it through the cockpit, and the pilot sits there and breathes it.

Some of the pilots wear oxygen masks; some of them don't. But it seems to me that we can create an effective payback to the taxpayer for the investments in these kinds of research facilities by addressing problems like that and actually performing an epidemiologic study in the area of pesticides where a man sits in a fixed chamber and you have the opportunity to look at physiological responses.

As experimenters, we are very fortunate. The man is sitting in a seat relatively still. The EEG, respiration, and cardiac functions can be monitored quite easily. The Air Force has 30 years of clinical background experience in this kind of an area.

I am advocating that we take other interdisciplinary sciences and join them into the health effects area to look at the types of dosimeters and exposure devices we have here today, to merge medicine into computer science and into epidemiology, and to bring these disciplines together in a coordinated fashion in a public health initiative.

I would like to identify that one area that stands out here, because I see a lot of opportunity for a simple study with immediate payoff. I see a lot of technology here, and it gives me the impression that it is untapped and unapplied, yet the potential is staring us in the eye. I think it is incumbent upon this conference to somehow pull these attributes together.

A second point might be: How could we pull these attributes together; that is, to take advantage of the knowledge that we all have to offer and that we all have to gain and learn? I might like to make a suggestion here because I have had the feeling that many of us are doing our own thing. Many of us appear to be running in opposite directions. We have the organic chemist who is in the corner doing his thing, and we have the physiologist in his corner doing his own thing. Wouldn't it be more effective if we could all communicate in a professional manner through the formation of--for a better choice of words--a society for personal monitoring in health effects? Why not have an organization of the interdisciplinary sciences of medicine, epidemiology, computer science, biomedical engineering, organic chemistry, biochemistry, and microbiology? Why would we advocate such a position? I can reflect over the last 20 years. I have seen many new disciplines come into being, which showed the same symptoms that this conference is showing here today; that is, there being a somewhat unfocused direction and the embryonic signs that here is a whole new discipline emerging before us.

So, I would think that one of the ways to pull this together would be to establish such a society and to follow it up with a professional journal, where the experience and research results can be published, at least on a quarterly basis. It would also help to have the different Federal agencies and industries provide a society of this kind with seed money to help it along and to further implement the educational processes of that new interdisciplinary hybrid, the environmental scientist. For example, the environmental scientist who may have an organic chemistry background may also have an epidemiologic background.

So, if we can shape and train these people in an academic environment, 10 years from now we will have the kinds of disciplines and the kinds of talent out in the field that can effectively respond in a coordinated fashion to solving problems in environmental health effects.

It is rather obvious to me that we are not going to come up with solutions overnight. I see this as a long-term effort. And the need will exist as long as technological man walks the earth.

So, I think it is incumbent upon this conference and future conferences to seriously consider formally organizing such a society so we can provide feedback to the Federal agencies which might be providing the funds to do this kind of work and to do this kind of research for the increase of knowledge in health effects.

I must also include the area of microcomputers. I think that there lies in this area a great opportunity for all of the disciplines, particularly in organic chemistry and membrane technology. From that standpoint, we should be looking at the other disciplines to learn what has been done in the last 20 years.

For example, there has been a lot of membrane technology displayed here today. But if we look into the field of medicine, you will find that in the design of artificial kidneys, in the design of blood oxygenators and artificial hearts, there is a widespread knowledge of membrane technology and ion specific electrodes.

In summary, that is my recommendation and observation. Thank you.

MAGE: Thank you very much, Matt. Our next speaker is Dr. Manny Shaw of the Interscan Corporation.

SHAW: I do have a few things that I want to say. But just before I get into that, I would like to say that in regard to the SO_2 dosimeter--as soon as we have a CO dosimeter, we will have an SO_2 dosimeter. The SO_2 instrument we are now making is a portable monitor. It is our second largest selling instrument. So, there is no problem--not just for us, but for some of the people who are making this type of a device. It is here now if you want it.

It has been stated by a few of the people here who are the instrument makers that they had hoped that the purpose of this meeting would be to make a beginning of an understanding between EPA and we who have to make, develop, and market these instruments. I think they are leaving today with a notion that that hasn't been done as yet. Hopefully, in the last hour or so that remains with us, and possibly with the idea that Mr. Petrovick had expressed of working together through an actual society, that might be the way to go.

Even prior to that, however, there are some things that can be done. Now, I have been in the instrument world for some time. Long before I ever got into the instrument world, I was in the technical research world. One of the things that I have noticed in particular with instruments, going back a decade in regard to instruments that have been developed for air monitoring, is that there is a very large credibility gap between such agencies as EPA and other agencies who are responsible for this type of monitoring and the industry which is supposed to be making these instruments.

I think that we have all been through the experience of using an instrument that is supposed to be the answer to everything, and is going to do this and is going to do that, and then it doesn't seem to work out too well after it is tested. We have all been through this process, and I know that EPA in particular has gone through this. What I would like to do is to put forward what I think is the reason for this. Now, I must preface my remarks with the statement that it only represents my thinking. I am not speaking for any other instrument maker or manufacturer here.

The development of the credibility gap starts off with the fact that in industry we have our engineers who are competent and capable, and maybe some who are incompetent, but no more or no less than what you have at EPA. We also have our research people, our scientists. I spent 20 years doing that. So, I feel I can speak from both teams, you might say.

What happens is that these scientists and engineers work in their labs and on their drawing boards, and they come up with a concept. They work on it. They work on the circuits. They work on the plumbing and whatever. They have something that seems to work. And it is field tested, or sometimes they don't field test it or they are not allowed to field test it--it all depends. But it looks as though they have got something that they can now go out and sell.

Now, at this point it largely gets out of the hands of the scientists and the engineers, and it goes into marketing. It has to go to the people who now have to go out there and sell. What happens when you are out there to sell, is that we all seem to be thinking along one line: "We need this kind of instrument, so not only is my company going to look to do this, but you can expect that there are the other companies with their smart engineers and their smart scientists who will do the same."

This device is turned over to the marketing people and the sales people, and they now have to compete. I don't think it is any stretch of the imagination to say that sometimes as a result of this need to compete, they may leave out certain facts about the device in sales pitches. They may imply a certain fact, or maybe they believe what they want to believe.

I admit that it will happen and does happen. I don't say it is a deliberate snow job. I wouldn't use any word that strong. But as a result of the fact that you have to compete with somebody else who is coming up with a related idea, some of your people who are not trained technically may only get certain information from the lab before they go out. Maybe they didn't quite understand it, and so they give the erroneous information. As a result, you get confusion in the user or the man at EPA or some other regulatory agency who has to check this instrument out.

Another difficulty, I think, is that maybe the regulatory agencies are asking too much, and maybe the manufacturers are promising too much. I think that is another big difficulty.

There is a need for these two groups of people to work together. There is a need to discuss the state-of-the-art. I mean, what actually is the state-of-the-art? What are we really able to do? Are you able to live with this?

I think if we did that, we as instrument makers may be a little surprised. Maybe some of these agencies could live with us, at least until the next step is taken. I think another thing is that possibly maybe the agencies themselves aren't too certain about what they want--maybe because they don't have enough information as to what is needed, as to the relationship between something that they have to measure and some effect that they are looking for.

There is another difficulty, and I don't understand why it should be. That is the unrealistic demand for an instrument that will do many different things, and yet should cost $500 or less. It is interesting to note that when I first got into the portable-type instrument world, and that was 4 years ago, I heard about that same magic figure of $500.

I know that my house has gone up in real estate value since then, but there seems to be the idea that instrument costs don't go up. So, at least if they would say, "We want something for $650 or less," I could understand it.

The difficulty with even that concept is that if it is so cheap, it must be easy to make. This will not happen unless we are going to have some rare breakthrough. I have been in research, as I said, longer than 20 years--30 years--and I doubt if I have seen a real breakthrough. I mean one that you could really put your hands on except in the integrated circuitry community or that type of thing, microminiaturization.

So, if it is so cheap, it has to be something that is rather obvious. And if it were rather obvious, we would already have it. I think that is all I wanted to say to emphasize that point.

In review of all of this, I really would like to hear from some other instrument makers, because, as I said, I am not speaking for them. We are less organized as a group than you, the user community, are.

But there is a strong need for working together and really taking away the mask and all else that has stopped us from really knowing what can be done.

If we could hear from someone else, either from industry or from EPA, I would like to hear some remark on that.

MAGE: All right. I will be purposely brief.

It has been very rewarding to me personally to learn of the advances and technology in microcircuitry, especially for the physiological variables. It is a whole new dimension which I personally hadn't been knowledgeable of in considering alternate study designs.

In talking to epidemiologists, statisticians, and engineers at EPA, it is apparent that it is a dimension that we could enter into some of our study designs.

I think we are getting to the point where we could really start talking about using these devices in real life. The applications are there. We have a lot of air pollutants in our environment of which the health effects are beginning to be guessed at, particularly carcinogens and toxic materials. We also have the whole problem of long-term exposures to low levels of pollutants.

We don't have any 5-year standards or 10-year standards or 20-year standards. And one could very well ask, why not? Certainly if you are looking at cancer or some kind of systemic disease caused by a buildup of lead, mercury, or cadmium, why shouldn't we have a 20-year standard for them? I don't know.

I think it is something that we can consider, and I think in order for us to do it with some statistical background, random personal sampling might be very important. That is a common technique in order to determine something about a distribution. You don't have to sample every ballbearing or measure its diameter. Or if you are with the Government Services Administration and you are accepting a shipment of pens from a company, you don't have to sample every pen. You take out a random sample and you look at the percentage of failures, and you make observations about the percentage of defective ones in the population. With that same kind of analysis, we can do the same thing in regard to the percentage of endangered people.

If we are concerned with long-term exposures to low levels, we could take people out, sample them, and make probability statements about the distribution in the entire population.

So, I personally feel that there is a need and a use for personal monitors, both passive and active. In the Agency right now, at the top of the pyramid--I am at the bottom--is work with toxics and carcinogens. We have criteria pollutants and noncriteria pollutants which are of long-standing concern to us. But the way our Agency works is that we are a fire-fighting organization. Once a fire is put out and we have set a standard, immediately the other immediate problems take our maximum attention and interest.

And someone who is left out there putting down the embers, developing an instrument for yesterday's pollutant, suddenly asks, "Where is everybody?" Everybody is now worried about a carcinogen, while that person is still fighting carbon monoxide or NO_2.

But I think overall there is a tremendous opportunity with the miniaturization and development of personal monitors for us to expand our knowledge of what the population exposures are.

I think we can use portable monitors, and I am not worried about the cost in that matter, because you can take a $5,000 instrument and you can get 10 people to wear it over 20 days each. That is 200 days out of the year that you can sample people using a good instrument. If you have a proper study design, the economics may not be a stumbling block. And I am going to try, within our Agency, to see if there isn't some way that we can get around this $500 threshold that people seem to feel that they have to have.

I think quality is important, and quantity, perhaps, might be secondary.

I think that we have a lot of concern. As Matt pointed out, the pesticide problems are real. There is a need there. The Agency is responsible for setting emission standards and usage standards for pesticides and for toxic materials. In many cases, people have to make cost benefit evaluations, and they have to guess the exposures.

If this is a completely new pesticide that somebody wants to apply, EPA might only know what the half-life of a pollutant of a similar chemical structure is in the atmosphere. EPA doesn't have the luxury of time to do the studies because it has to make a decision. It may make guesstimates that "this new one is similar to an old one seen before which had a half-life of 5 days in the environment. We will estimate that it also has a 5-day half-life." They make estimates of the number of people who are exposed and estimates of the health effect. It would be so much better if we had some pieces of real hard data from personal monitors that we could use in the analysis. If we do it properly, we can analyze the data and make reasonable interpretations of the results.

I would like to say also that I am very pleased to see the developments that industry has made. A lot of these developments were done without Government support and without Government direction. There has been a tremendous advance in technology. I am very pleased personally to see that there is so much available that if I had the budget, I could use most of it.

But I think within our own realm of Federal Government, we have so many agencies--ranging from the Bureau of Mines, which is in the Interior; NBS, which is in Commerce; Energy, EPA, the Office of Naval Research, which are worried about pollutant buildups in submarines; NASA, which is worried about pollutant buildups in sealed spacecrafts--that industry should have some closer workings with us, perhaps, because there is a lot of duplication. We can continue to have conferences like this one. And I am sure that there are people who are working with personal monitors within the Government and some Government agency that we have not invited to attend.

However, I think we have a lot to do to organize it so that at least those agencies which are going to use personal monitors for whatever purpose will be talking with one unified voice, so that you, the instrument maker, won't have one set of specifications from one agency and another set of specifications from another at cross purposes.

I would like to open the discussion up now for questions and comments from the audience.

DR. FRANCIS BERLANDI: Fran Berlandi, of ESA Laboratories. Speaking as a Certified Industrial Hygienist, there were a few statements made by the panel that certainly come as a surprise to me--that is, that "we do not have the sampling technology available to assess pesticide exposure in the field." I think that if you really do have clients, and you yourselves are interested in performing these types of measurements, you can contact me. I can put you in contact with other industrial hygienists throughout the country. These measurements can be made.

Secondly, there does exist a society that essentially expands itself across many disciplines. This is the American Industrial Hygiene Association (AIHA). It has bioengineering through a significant number of members in the society from the medical community. It addresses the computer sciences area. It has committees on analytical chemistry. It is probably one of the broadest based societies that exists in the United States.

I think that if you are really looking for a society for a group of individuals that does transcend the different disciplines, that you should address yourselves to the AIHA and take a look at its journal. I think the type of studies that were talked about here would readily be accepted in the journal of the American Industrial Hygiene Association. It is a monthly journal and has been out for 20 to 30 years. I would just like to have that on the record.

MAGE: Thank you very much, Dr. Berlandi.

DR. PHILIP WEST: I would address my remarks, I think, to Matt Petrovick. He has given us a lot of stimulating ideas.

I wonder if he knows what the crop-dusting pilot always does before he makes his flight? About the last thing he does before climbing aboard, he lifts his eyes to the sky and he says, "Let us spray."

I would like to be a devil's advocate for one moment: the only thing we ever talk about, it appears, are the hazards. Of course, the toxicologist seems to feel, and there may be some disagreement with this, that everything is toxic, and therefore hazard is associated with the concentration or the mass amount.

Among the things that we could look for in our monitoring data are beneficial things. This may be a little difficult for the animal world, but certainly in the plant world, the benefits of contaminated or even polluted air sometimes can be noted. I think we ought to keep our minds open.

Just because we can measure something in the parts-per-billion level doesn't mean that it is harmful; it may very well be beneficial. For example, we must have polluted air masses. Otherwise, none of us would be here. We have to have dirt in the air for condensation nuclei. Otherwise, you wouldn't have clouds. There would be no rain and no thunderstorms. If you had no thunderstorms, we would have no oxides of nitrogen in the air. Plants must have oxides of nitrogen. They get it from the air. A substantial amount of the nutrients for the plant world come from meteoric precipitation.

I don't know and I would like to have your opinion as to what extent does man benefit from trace constituents in the air that he breathes? It can't be all harmful. So, I just wonder if anyone has ever correlated air quality data with the general health of the population from a positive standpoint.

PETROVICK: I think you have made an excellent observation there, and I would find it very difficult to disagree with you. You are absolutely right; perhaps most of us are looking at the detrimental aspects of it.

I don't profess to be an expert in this area at all, but I think negative and positive research results are always fruitful. It is unfortunate that conferences like this sometimes get biased in the other direction. I completely agree with you that we have two sides to the coin. Many of the environmental constituents are absolutely necessary to the existence of life.

DR. ROBERT CHAPMAN: Maybe we should start setting up minimum daily requirements for pollutants.

PETROVICK: That reminds me--last night Dr. Chapman and I had a question addressed to us regarding minimum requirements or specifications from, I believe, one of the manufacturers. I think, if I am correct, that Dr. Chapman responded, "I am not going to give you those specs this evening." I think that that is an interesting reply, because from an engineering standpoint, I think it takes years and years to develop those kinds of specifications.

More importantly, as Dr. Shaw alluded to, it is very difficult to go back into your home laboratory, in the back pool room, so to speak, and design an instrument--a dosimeter, a physiologic box, whatever--without living in the exact environment of the user who is going to have to live with that device after you give it to him.

Until engineers, scientists, and epidemiologists can begin to communicate with each other at the very onset of the design phase and look at it from the user's standpoint, I don't think the acceptance of these devices is going to be too successful.

We see all kinds of devices coming out that were designed in the "back room," and we bring it to the physician, the epidemiologist, the chemist, or whomever, and they will say, "My gosh, this isn't what we talked about. I can't use this. It's too big," or, "My test subject won't accept it."

So, I think it is very difficult in a conference of this kind to lay down specifications and guidelines. Perhaps guidelines are easier. But what I believe is imperative is that our kinds of disciplines work with the user and with knowledge of the user's problems. Also, we must incorporate the users in the design of these devices so that when they receive them, the devices are going to resemble what was wanted, and they are going to work as expected. I think that is crucial.

CHAPMAN: I want to assure the gentleman who asked that question that I wasn't trying to be facetious in any way in the answer I made to him. We have a lot of talking to do in-house on this subject. We have to do this considerable talking for each and every type of pollutant that we can think of that might be worthwhile to study.

We have to get set in our own minds the types of physiological effects and the types of averaging time that we think would be most appropriate. I would think that we have to do a considerable amount of pilot testing before we commit ourselves or before we ask any manufacturer to commit himself on a large-scale venture. I think that this is relevant to what you were saying before, that we have to come to certain understandings about what to do next, and then next, and then next after that.

From our standpoint, I think the ideal way to do things is to let me test the instruments at various stages of development before anybody gets overcommitted or before anybody feels that he had something stuffed down his throat.

So, I would like to reassure everybody that I had not meant to be facetious in any way. We just have a lot of thinking to do ourselves before we know or before we can form a clear conception of what types of specifications would best suit us. That is all I was trying to say.

In response to Dr. West, to some of your observations of long ago, I have heard some anecdotal reports. I think they are largely anecdotal, that maybe ozone makes people feel better. I can't specify any more than that.

I accept that oxygen is an obvious example of something we need that is in the air. However, I expect that showing the beneficial effects of pollutants is going to turn out to be just as hard as showing harmful ones. But that is certainly not to say that there might not be some.

WALLACE: For the record, I did want to insert some comments made to me in letters from Dr. George Schnakenberg at the U.S. Bureau of Mines, who was unable to be here, but who, as you know, is another of the main supporters of personal monitor research, and some of the people he supported are here.

The Bureau has supported work at GE in developing its CO dosimeter. He states that: "...We are also funding the development of a similar sensor for NO and one for NO_2, with a goal of 1 ppm of NO and 0.1 ppm of NO_2 sensitivity respectively. The work should be completed by summer of 1979."

He also states that the work done by Dr. Palmes was supported by the U.S. Bureau of Mines.

MR. PAUL KIZAKEVICH: Paul Kizakevich from Research Triangle Institute. I would like to further support the suggestion that Matt made about the possibility of forming a society. I appreciate the comments that Dr. Berlandi made of an existing society that is there for industrial hygiene.

However, if we consider the scope of this conference on the subject of personal monitors alone, we certainly already have seen that there is a lack of communication between Government and industry, and probably to some extent among the different Government agencies--I am sure EPA, NIOSH, and the Department of Energy--and the academic community which was represented here in this conference.

But those are three aspects of research and development areas that certainly can be brought together. If the scope of environmental monitoring is limited to the context of personal monitoring, I think that not only is there justification for that type of organization, but I think the function of that organization to obtain maximum transfer of information will be attained.

Certainly in medicine there are multiple societies within each discipline. They exist, not because they each go off into a different area necessarily, but because the amount of information to be transferred is just too much for any single society to publish and handle.

Again in medicine, the problems of quality assurance and instrument development are very similar in the sense that often industry is not really attuned to what is required in the health measurements. Just as an example--the equipment required in the measurement of toxic substances by cumulative dosage, as opposed to exposure.

As a result, there are a lot of studies done just on the characteristics of the available instruments. I am sure that there have been companies made and destroyed (perhaps not totally justified) because of the evaluation between the true quality of the instruments, and at the same time, what their specifications were.

MR. ARNOLD GRUBER: I would like to say something in support of Manny Shaw, who had some comments from industry. I would like to thank both Manny Shaw and David Mage for their rather eloquent summations. I think they hit very nicely on my personal feelings as a representative from industry. I think they addressed the present problem as it currently stands. I am sure other people have some comments on that. But I would like to pass it up for now.

CHAPMAN: May I say one last thing? One area that I haven't heard discussed at all and that is certainly important from the standpoint of field uses is that I think we all need to make absolutely sure that the reagents used in the instruments do not turn out to be considerably more toxic than the substances they are designed to measure.

Indeed, they must be demonstrated to be nontoxic in any way so far as is possible.

MAGE: Yes. Safety, of course, is always of prime concern in anything that we do. And I am sure industry has that same concern.

KIZAKEVICH: To expand on Dr. Chapman's comment, I wonder if the new FDA regulations on medical device safety have any role to play in placing an instrument of any sort, medical or physical, on a person and have him carry it around?

PETROVICK: I think I can respond to that.

The movement by the Kennedy group has been attempting to pass legislation for medical safety, particularly in the area of medical instruments and sensors. Unfortunately, that legislation has been gyrating back and forth in Congress for about 5 years. However, it is coming closer and closer to fruition. I believe that FDA will not be able to get more than a labeling effort passed.

But I think what Paul Kizakevich is bringing up is something that we all should keep in mind, particularly the designers and manufacturers of personal monitors, and not necessarily only those devices that have to do with physiologic measurement, but also anything that may be attached to the attire of the human subject.

There may be new hazards that might not be electrical safety, but they may be, as Dr. Chapman is pointing out, chemical hazards. So, I believe we must look at both of those areas. This may be a serious challenge.

I have one last comment. Dr. Mage, do you have any reflections on when another conference of this kind might be in the offing? Is there any planning through your group and committee to keep the ball rolling?

I think it would be a shame to let the momentum of this knowledge base that we have generated here in the last few days go to waste.

I just wondered what the future plan is for perhaps having another meeting, say, within a year?

MAGE: I don't think there is any plan per se, but I think that certainly Brookhaven, EPA, and other Government agencies which have been holding their own conferences independently, are now talking to each other. I think there is every probability of having another meeting, and I certainly will recommend it. You know, there is no guarantee that funding for a conference will exist in my Agency. But I certainly will recommend that we allocate funds and hopefully get an interagency workshop sponsored, not only by EPA, but by DOE, EPA, U.S. Public Health Service, NIOSH, and all of the agencies that sponsor work on personal monitors. I think that Dr. Stacy in his remarks yesterday was very cogent, because it doesn't do any good to sell me or Dr. Wallace or anybody else here. We have to sell people in Washington, D.C., who will not only recognize the need for personal monitors, but also the problems and the difficulties, and who will have the patience to support long-term research.

An epidemiological study is not a short-term thing. As the Harvard group pointed out, they have been going now some 3 years. Now, the results are in process. The data are there. It takes a long time to evaluate it. You have to develop statistical techniques to handle all of these data and to handle the interferences and cofactors such as smoking, correction for age and sex, and the lack of sex, or what have you.

So, I think there certainly is a very important reason for Government agencies to work together on this.

I will certainly make informal recommendations through our interagency contacts, which I hope would result in a formal recommendation from several different agencies for an interagency type of sponsorship. It would be very nice if we could have such a meeting every year. I think it would certainly be beneficial for us all to meet again on a yearly basis just so that we can see the promises being fulfilled.

Bob Beadles talked about the geometric progression in computer capability. Things are now becoming smaller and microsized. I think there is a tremendous growth rate in this area, and an annual type of meeting would be very valuable to us for keeping up. I am sure that our colleagues in education, Government, and industry would be very receptive to this.

PETROVICK: I would like to reflect on the element of support for future meetings. I happened to read the House bill that Congressman George Brown left with us. In one of the paragraphs, it stated that part of the $7 million that is going to be allocated should be allocated for the purpose of communicating new knowledge and new science in terms of holding conferences and going to meetings. I think that the answer lies right there if the bill passes. We must make sure that a conference can access that kind of support.

MAGE: Yes, the mechanism is there. As Congressman Brown pointed out, he is on our side. He wants us to get information, not just to show that our standards are correct or incorrect, but to show that our standards are reasonable. We have to be able to recognize that sometimes mistakes can be made in the interpretation and collection of data. And we have to be willing to say, "Yes, we were wrong, our standards are too strict." Or we have to have the courage to say, "They are not strict enough." We can only do this if we have defensible, reasonable data.

WALLACE: I would like to add my voice to the general acclaim for Mr. Petrovick's idea of forming a society, and to make the additional point that we now have a mailing list that includes a very good representation of the users, manufacturers, and persons concerned with the physical-chemical side of it. We don't have a mailing list representing the physiological side. Perhaps Mr. Petrovick could provide us with that. We may be a little weak on the microcomputer and bioengineering sides.

Once we have found the intersections of several collections of that sort of names, we might be able to send out flyers containing information on the results of the conference and any suggestions that you might have.

PETROVICK: I appreciate that comment very much. I think we can supply such a list.

I would like to mention an experience I had after the first of the year at an international conference in Hawaii. This was an international conference sponsored by the University of Hawaii's Department of Electrical Engineering, Biomedical Engineering, Computer Science, and the medical community, both private and industrial. We had the opportunity through a paper presented there to make this society aware that EPA is involved in health effects. There were many professionals from HEW, NIH, academia, and so on from all the disciplines--really a broad coverage.

Most of the people at that conference happened to have a total unawareness of EPA's involvement in health effects. In fact, they weren't even sure what health effects happened to be of concern to EPA.

As a result of that, I made a further report in order to indoctrinate the meeting sponsors to this effect. During one of the planning committees, it was requested that EPA cosponsor part of the international conference next year, particularly with a full day's session on environmental health effects--that is, those aspects of medicine, epidemiology, air dosimetry, computers, and engineering that pertain to personal monitors.

Here we have the opportunity to interface with other societies on an international scale. I think that is another reason why I feel so strongly that we shouldn't let this communication capability slip through our hands.

We should be absolutely sure to make future contact with the other disciplines, because why should we reinvent the wheel? There is a lot of knowledge that is already out there. I think it would behoove us to try and apply that knowledge to health effects.

MAGE: Thank you very much. I declare this meeting adjourned.

Utility of Passive Personal Samplers for Measuring Ambient Air Pollution*

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A passive sampler is one which requires no power or flow regulators to cause or control movement of air through the sampling medium. The present generation of passive samplers is made up of integrating devices which permit measurement of average concentrations for the period of exposure and which are not designed to measure peak concentrations. It might be possible in the future to develop passive samplers which react with the contaminant gas in a reversible manner--e.g., by absorbing or adsorbing larger quantities at higher concentrations--and which use self-contained readout or alarm systems to indicate instantaneous concentrations. The development of such devices has not yet been reported.

The passive personal samplers described in the literature depend on transfer of the contaminant gas to a suitable absorbent by diffusion through an air column of known dimensions or by permeation from the atmosphere through a well-characterized membrane to a suitable collecting medium. The principle on which both types operate is that of the concentration difference acting as the driving force and the diffusion or permeation barrier acting as a resistance controlling the flux through the barrier. In the case of an air column, this flux can be estimated if the dimensions of the column are known, since the coefficient of diffusion of a particular gas molecule in air can be estimated by a variety of techniques. The state-of-the-art in membrane fabrication appears, however, not to be sufficiently developed to permit the independent measurement of a permeation constant for a particular membrane for a particular gas. The membrane devices, therefore, require individual calibrations.

The chief advantages of the diffusion or permeation samplers are that they are routinely of low cost, are very lightweight, require no maintenance, and are simple enough to be used by untrained individuals insofar as the sample collection is concerned. It should be stressed here that the devices that have been described in the literature are sampling devices and are not complete analytical systems. All require the removal of the gas from the sampling medium and analysis by trained personnel. In each case, the quantity of contaminant collected is calculated in terms of equivalent concentration x time (ct) units, and the time-weighted average (TWA) concentration during the exposure is obtained by dividing by time of exposure.

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*Editor's Note: This summary on the use of passive personal samplers for measuring ambient air pollution was prepared for presentation as a part of the preceding panel discussion and is therefore included in these Proceedings even though Dr. Palmes was unable to attend the panel discussion.

The sampling rate can be varied over very wide ranges by changing the cross-sectional area and/or the length of the diffusion or permeation barrier. Additional flexibility as to the required exposure time can be achieved by choice of the final analytical procedure. In the design of the sampler, therefore, it is first necessary to choose the sampling interval. If the devices are to be used as personal samplers, one must be reasonable in this choice. The expectation that an individual, even if equipped with a group of small, lightweight samplers, is going to be willing to change these (or have them changed) on an hourly basis with the accompanying recordkeeping requirements, is not realistic. On the other hand, it might be quite acceptable to the user to keep a sampler on or near his or her person for a full week and record only the time that sampling was started and stopped. In any event, these are the types of considerations that must go into the selection of the sampling interval and, accordingly, the dimensions of the passive sampler.

In addition to limitations on measuring peak concentrations, it should be pointed out that passive samplers will only be useful for atmospheric gases, not for particulates. The reason for this is quite simple in that both the air column and the membrane types depend essentially on Fick's First Law of Diffusion. Although particles do diffuse, they do so at rates that are several orders of magnitude lower than those of gases. Thus, the collection of any significant quantity of even the smallest particles (which have the highest diffusion coefficients) is not theoretically possible. The obverse of this coin, however, is that when one collects a sample and analyzes for a specific element, one can be sure that the element collected was in the environment in the gaseous form and not as a particulate.

The only published results on use of passive samplers for measurement of ambient gas levels are those of Palmes et al. (1976) and Melia et al. (1978), in which the NYU sampler was used to measure the concentrations of NO_2 in dwellings to determine the differences in those with gas or electric stoves. In both of these studies, the samplers were exposed continuously from 4 days to 1 week and measured NO_2 concentrations from approximately 0 to somewhat above 50 ppb, the U.S. Primary Air Quality Standard (annual average). Although the results have not been published, West (1979) stated that the permeation devices for SO_2 which Reiszner and West reported in 1973 have been used for measuring SO_2 concentrations for periods of 2 weeks to a month. This was done by catalytically stabilizing the sulfite complex, permitting its analysis at some time after the completion of sampling.

Although results have not been reported for other gases of importance as air pollutants, it appears that hydrocarbons could be determined very readily by a number of the diffusion or permeation devices using charcoal as the adsorbent and separating the collected gases by gas chromatography. No sampler has been reported for ozone, but its very marked chemical reactivity should certainly permit its estimation after collection in a passive sampler. An NO_x sampler which can be used in conjunction with the NO_2 sampler reported in this symposium can be used to estimate the relative contributions of NO and NO_2 to the NO_x. This device (Palmes et al. 1979) as presently designed, however, would not permit measurements for the 1-week period for which the NO_2 sampler was used. Finally, the quantitative estimation of CO by passive samplers has not yet been accomplished, although it certainly should be feasible.

It should be mentioned that there appears to have been very little interest in personal sampling in the air pollution field until very recently. Most of the work in sampling and analysis has been focused on measurement of concentrations in large air masses and the dispersion of those air masses. The major effort appears to have been aimed at emission control rather than the measurement of the exposure of individuals, and that estimation of dose to the individual has been very much neglected. One of the cardinal rules in industrial hygiene is to collect breathing zone samples because these are of the greatest value in protecting the health of the workers. It is obvious that this philosophy has lead to the development of a large number of miniature personal sampling devices for the worker. These, whether active or passive, were usually designed so that the exposure could be measured of a worker for a shift. For the immediate future, it appears, therefore, that sampling the personal environment of individual citizens for air pollutants will depend very largely on spin-off from research which was primarily motivated by the need to measure exposures in the workplace. This raises some serious questions as to appropriateness of priorities assigned to these two aspects of air pollution instrumentation research.

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